

Errata

<u>Page</u>	<u>Line</u>	<u>For</u>	<u>Read</u>
20	17	environment	environments
20	21	bath	batch
25	23	aporoach	approach
26	11	collid	collide
34	27	solution	suspension
39	1	flocculents	flocculants
53	4	velocity	flowrate
55	21	dynes/cam	dynes/cm
91	1	present	presence
120	1	$\rho = \frac{c \sin \xi}{\cosh \xi - \cos \eta}$	$\rho = \frac{c \sin \eta}{\cosh \xi - \cos \eta}$
125	22	compres	shows
125	23	with	and
132	17	F =	F ₂ =
151	18	$V_R = \frac{8a \psi_0^2}{2}$	$V_R = \frac{\epsilon a \psi_0^2}{2}$
157	7	0 < P < ∞	3 < P < ∞
163	2	$1.77 \frac{2\pi}{\lambda}$	$1.77 \frac{2\pi}{\lambda_c}$
170	2	stream potential	stream function
172	3	ψ_p	ψ
172	16	(3.115)	(3.113)
199	15	y → ∞	x → ∞
202	26	r _p = r _c	r _b = r _c
228	16	dv ₁ = S _{ABC} · d _r	dv ₁ = S _{ABC} · dr
233	9	A _n	a _n
233	9	B _n	b _n
259	33	Goren, S. L. (1971) Chem. Eng. Sci., <u>21</u> , 1151.	Goren, S. L. (1970) J. Fluid Mech., <u>41</u> , 619.

SEPARATION OF FINE EMULSIFIED OIL
PARTICLES BY DISPERSED AIR FLOTATION

A Thesis submitted to the
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ABSTRACT

In this study the separation of minute oil particle (diameter $< 10\ \mu\text{m}$) from dilute solutions (concentration $\approx 150\ \text{ppm}$) by dispersed air flotation was investigated. The main purpose of this work was to assess the floatability of oil particles in this range of sizes and therefore avoid usage of a coagulation stage prior to flotation. A systematic study of different chemical and physical variables including pH, surfactant and salt concentration, particle and bubble size on the kinetics of the process was carried out.

A first order rate equation was found to fit adequately the experimental results. The rate constant, which is a measure of the flotation rate, was found to vary as 0.5 power of the particle size for particles between $1\text{--}4\ \mu\text{m}$ and bubbles below $350\ \mu\text{m}$. The experimental results showed a reduction in the rate constant as the electromobility of the oil particles increased. The effect of bubble size was also investigated experimentally and it was observed that the flotation rate decreased for increasing bubble sizes.

The theoretical part of the work included a study of the collision efficiency of a single bubble based on the grazing trajectory approach. Interactions due to intermolecular forces as well as corrections to hydrodynamic forces were incorporated in the equations of motion of a bubble-particle system. The theoretical results for the efficiency obtained here were lower than those predicted by simplified hydrodynamic models reported in the literature. The efficiency was found to vary as -1.5 power of the bubble size for oil particles. This dependence was checked through experimentally predicted values of efficiency and good agreement was found.

To Mojtaba and my mother

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<u>TABLE OF CONTENTS</u>	PAGE
Abstract	2
Acknowledgement	4
Table of Contents	5
List of Figures	9
List of Tables	12
CHAPTER 1 Introduction	14
CHAPTER 2 Experimental	38
2.1 Introduction	38
2.2 Experiments and Techniques	45
2.2.1 Flotation Apparatus	45
2.2.2 Bubble Generation Device	47
2.3 Materials	55
2.3.1 Water	55
2.3.2 Oil	55
2.3.3 Salts	55
2.3.4 Surfactants	56
2.4 Preparation of the Emulsion	59
2.4.1 Ultrasonic Homogeniser	59
2.4.2 Modified Ultrasonic Homogeniser	60
2.5 Bubble Size Measurement	61
2.6 Particle Size Measurement	65
2.6.1 Microscopy	65
2.6.2 Light Scattering	66
2.6.3 Coulter Counter	66
2.6.3a Calibration of the Instrument	68
2.6.3b Measurement of Particle Size Distribution	68
2.7 Microelectrophoresis Apparatus	73
2.8 Preliminary Experiments	74
2.8.1 Experimental Procedure	74
2.8.2 Analysis of the Flotation Results	75
2.8.3 Effects of Salts	78
2.8.4 Effect of pH	79
2.8.5 Discussion on Preliminary Results	80

2.8.6	Choice of Surfactant	87
2.8.6a	Cationic-Anionic	89
2.8.6b	Nonionic-Anionic	91
2.8.6c	Nonionic-Cationic	91
2.8.6d	Cationic-Nonionic	92
2.8.6e	Single Surfactant System	94
2.9	Flotation Experiments	97
2.9.1	Experimental Procedure	97
2.9.2	Surfactant Used	98
2.9.3	Gas Flowrate	99
2.9.4	Effect of pH	100
2.9.5	Concentration of Surfactant	100
2.9.6	Effect of Salt Concentration	101
2.9.7	Effect of Bubble Size on the Rate of Flotation	104
2.9.8	Study of Coalescence of the Particles in the Flotation Column	107
2.10	Discussion	109
CHAPTER 3	Theoretical	111
3.1	Introduction	111
3.2	Hydrodynamic Forces in Two Spheres System	117
3.2.1	Motion of Two Spheres along their Line of Centres	121
3.2.2	Motion of Two Spheres perpendicular to their Line of Centres	129
3.3	Intermolecular Forces	140
3.3.1	Disjoining Pressure	140
3.3.2	Electrokinetic Phenomena	143
3.3.2.1	The Electric Double Layer	143
3.3.2.2	Distribution of Potential in the Double Layer	145
3.3.2.3	Potential Energy of Interaction between Two Flat Surfaces	148
3.3.2.4	Potential Energy of Interaction between Two Spherical Particles	150
3.3.2.5	The Repulsion Force between Two Spheres	151
3.3.3	The London-van der Waals Attraction	152
3.3.3.1	The London-van der Waals Attraction between Two Spherical Particles	153
3.3.3.2	Retarded London-van der Waals Forces	156
3.3.3.3	Calculation of Retarded Forces for Two Spheres	158

3.3.3.4	Calculation of the Correction Factor	161
3.3.4	The Total Potential Energy of Interaction between Two Spheres	163
3.4	Motion of a Sphere in a Viscous Fluid	167
3.4.1	The Virtual Mass	168
3.4.1.1	Calculation of Kinetic Energy	170
3.5	Solution of the Equations of Motion of Two Spheres	175
3.5.1	Grazing Trajectory	181
CHAPTER 4	Results and Conclusions	187
4.1	Experimental Results	187
4.1.1	Dependence between Rate Constant and Particle Size	190
4.1.2	Dependence between Rate Constant and Bubble Size	192
4.2	Theoretical Results	193
4.2.1	Dependence between E_c and Bubble Size	197
4.3	Discussion	198
APPENDICES		209
1.	Different Techniques tried for Preparation of Emulsion	209
2.	Bubble Photography Devices	213
3.	Settings for the Coulter Counter	214
4.	The Bipolar Coordinates (ξ, η, ϕ)	215
5.	Conversion of the Boundary Conditions from Cylindrical Coordinates into Bipolar Coordinates as used in Section 3.2.1	217
6.	Obtaining Equations (3.38) - (3.40) from the Boundary Conditions in Section 3.2.2	219
7.	The Expressions for the Coefficients of $A_n, A_{n-1}, B_{n+1}, B_n, B_{n-1}$ in the Continuity Equations (3.45) of Section 3.2.2	222
8.	Integration Procedure for Calculation of London-van der Waals Potential between Two Spheres	228
9.	Constants in the Expressions for Potential and Force of Attraction (3.91) and (3.93) in Chapter 3	230

10. Mathematical Procedure to obtain Equation (3.112) from (3.111)	232
11. Calculation of the History Integral	234
COMPUTER PROGRAMMES	237
1. BUBBLE	237
2. COULTER	238
3. TRAJ1	240
4. TRAJ2	244
5. VIRTUAL	255
References	258
List of Symbols	265

<u>LIST OF FIGURES</u>	<u>PAGE</u>
2.1 Schematic diagram of the experimental set-up	46
2.2 Bubble generation device	48
2.3 Effect of vacuum in the suction line on the amount of gas entrained	50
2.4 Effect of upstream liquid pressure on the amount of gas entrained	50
2.5 Effect of vacuum in suction line on the amount of gas entrained for different liquid pressures	51
2.6 Effect of vacuum in suction line on bubble size	52
2.7 Effect of upstream liquid pressure on bubble size	52
2.8 Gas chromatography analysis of impure sample of Ethoquad 18/12	57
2.9 Gas chromatography analysis of purified sample of Ethoquad 18/12	57
2.10 Gas chromatography analysis of impure sample of Ethoquad 18/25	57
2.11 Surface tension of solutions of Ethoquad 18/25 in distilled water	58
2.12 Photograph of bubbles	62
2.13 Bubble size distribution in the flotation column	63
2.14 Bubble size distribution on log-probability scale	64
2.15 Photomicrograph of oil particles	69
2.16 Particle size distribution in the flotation column	70
2.17 Particle size distribution on log-probability scale	71
2.18 Cumulative volume of oil particles vs. particle size as measured by Coulter Counter	72
2.19 Plots of $\ln(C_o/C)$ vs. time for experiments in tap water (surfactant CTAB)	76
2.20 Plots of $\ln(C_o/C)$ vs. time for experiments in distilled water (surfactant CTAB)	76
2.21 Flotation rate constant vs. salt concentration (surfactant CTAB)	81
2.22 Flotation rate constant vs. salt concentration (Na_2CO_3)	82
2.23 Bubble size vs. CTAB concentration	83

2.24	Bubble size vs. sodium sulphate concentration (surfactant CTAB)	83
2.25	Bubble size vs. pH (surfactant CTAB)	83
2.26	Electromobility of oil particles in solutions of CTAB in distilled water	86
2.27	Electromobility of oil particles in solutions of Ca Cl_2 in distilled water	86
2.28	Bubble size vs. surfactant concentration (surfactant Ethoquad 18/25)	102
2.29	C.M.C. determination for Ethoquad 18/25	103
2.30	Flotation rate constant vs. sodium sulphate concentration (surfactant Ethoquad 18/25)	105
2.31	Bubble size vs. sodium sulphate concentration (surfactant Ethoquad 18/25)	105
2.32	Electromobility of oil particles vs. sodium sulphate concentration (surfactant Ethoquad 18/25)	106
3.1	System of coordinates for axisymmetrical motion of two spheres	122
3.2	System of coordinates for asymmetrical motion of two spheres	122
3.3	Variation of disjoining pressure vs. film thickness, after Blake and Kitchener (1972)	142
3.4	The physical presentation of an electric double layer according to Stern's theory	146
3.5	The geometric presentation of Derjaguin method for calculation of repulsion forces	146
3.6	Correction factor for calculation of retarded London/van der Waals forces for two equal spheres separated by a distance S	162
3.7	The potential energy of interaction between an oil particle and a bubble	166
3.8	Values of K in the expression of virtual mass vs. distance of separation between two equal spheres	174
3.9	The geometry of two arbitrarily moving spheres	176
3.10	Flow diagram for trajectory calculation	185
3.11	Grazing trajectory of a particle approaching a bubble	186

4.1	$\ln N_0/N$ vs. time for flotation in distilled water	188
4.2	$\ln C_0/C$ vs. time for flotation in tap water	189
4.3	Rate constant vs. particle size for different flotation experiments	191
4.4	Collision efficiency vs. K_F	194
4.5	Collision efficiency vs. particle to bubble size ratio	196
4.6	Collision efficiency vs. bubble size	196
4.7	Plot of $E Ra^2$ vs Pe/Ra^3 for different aspect ratios, Ra , after Prieve and Ruckenstein (1974)	205
A1.1	Modified ultrasonic emulsifier	212
A2.1	The modified photography set-up	213
A4.1	Bipolar coordinates	216
A4.2	Spheres in bipolar coordinates	217
A8.1	Attraction between an atom and a sphere, after Hamaker (1937)	229
A8.2	Attraction between two spheres, after Hamaker (1937)	229
A11.1	Procedure for calculation of the history integral	236

<u>LIST OF TABLES</u>	PAGE
2.1 Specifications for different venturis studied	49
2.2 Performance of two of the venturis studied	54
2.3 Rate constants for distilled and tap water at different surfactant concentrations (surfactant CTAB)	77
2.4 Analysis of London tap water	78
2.5 Flotation rate constants for different concentrations of Na Cl	79
2.6 Effect of pH on flotation rate constants (surfactant CTAB)	79
2.7 Electromobility of oil particles in tap and distilled water	84
2.8 Electromobility of oil particles in tap water and distilled water + salt	87
2.9 Electromobility of oil particles in 20 ppm Ethoquad 18/12 solution	97
2.10 Effect of surfactants on the rate of flotation	99
2.11 Effect of gas flowrate on the rate of flotation	99
2.12 Effect of pH on the rate of flotation (surfactant Ethoquad 18/25)	100
2.13 Effect of surfactant concentration on the rate of flotation (surfactant Ethoquad 18/25)	101
2.14 Effect of bubble size on the rate of flotation	104
2.15	107
2.16 Coalescence of oil particles	108
3.1 Correction factors for motion of two spheres along their line of centres	126
3.2 Correction factors for motion of two equal spheres approaching each other along their line of centres	127
3.3 Correction factors for axisymmetric flow of two almost touching spheres	127
3.4 Comparison of exact and approximate solutions for motion along the line of centres	128

3.5	Correction factors for motion of two spheres perpendicular to their line of centres	136
3.6	Comparison of the results for motion perpendicular to the line of centres for two equal spheres	137
3.7	Comparison of results for motion perpendicular to the line of centres for two unequal spheres	138
3.8	Comparison of exact and approximate solutions for motion perpendicular to the line of centres	139
3.9	Values for kinetic energy for two equal spheres moving along their line of centres	173
4.1	Values of q in the relation $k \propto d_p^q$ for different experiments	192
4.2	Collision efficiency for a bubble and an oil particle	199
4.3	Percentage of oil removal in the flotation column for different experiments	207
A3.1	Coulter Counter settings	214
All.1	Method used to calculate the history integral	236

CHAPTER 1

Introduction

In this chapter a general outline of experimental and theoretical studies carried out on flotation is presented. In particular, special attention is given to those works of more relevance to effluent treatment.

Most of the separation processes, i.e. sedimentation or filtration employing conventional filters, become inefficient and uneconomic when the concentration of materials in suspension is low. A group of methods known as foam separation techniques or adsorptive bubble separation techniques have proved to be efficient in these cases.

These methods are based on the generation of foam and adherence of the suspended materials to the gas-liquid interface with subsequent mechanical removal of the foam.

Different bubble separation methods have been classified by Somasundaran (1972) on the basis of mechanism of separation and size of the suspended materials.

Froth flotation is one of these methods and is widely used in mineral beneficiation processes. As bubbles rise through the pulp (suspension), they collide with the particles which can consequently be collected. In order to stabilise the froth layer, chemical additives known as "frothers" are normally added to the suspension. Also, to impart floatability to the particles, surface active materials ("collectors") are employed. Collector molecules generally contain a polar and a non-polar or hydrocarbon group. The acquired hydrophobicity is the

result of adsorption of these reagents on the particles' surface with their nonpolar end oriented towards the bulk solution.

Other chemicals used, in particular in microflotation processes, to remove colloidal particles in effluent treatment are "coagulants". These are hydrolyzing metal salts (aluminium or ferric salts) which destabilize the colloidal matter within a given pH range and make the flotation process more efficient (Cassell et al, 1968; Mangravite et al, 1975).

Different flotation processes have been classified according to the method used to produce the bubbles. These are: dispersed air, dissolved air and electro-flotation. In dispersed air flotation, bubbles are formed by either the shearing action of propellers or by passage of gas through a porous material into the liquid. The bubble size in the former case is about 0.5 - 2 mm and the technique is widely used in mineral flotation (Taggart, 1945; Klassen and Mokrousov, 1963) where both agitation and large bubbles are needed to keep the particles in suspension and to be able to lift rather large particles. Bubbles as small as 50 μm are produced by blowing air through a porous glass frit containing concentrations of up to 0.5% V/V of a short chain alcohol. This procedure has been used for removal of colloidal matter from pulps in laboratory scale (Cassell et al, 1971; Mangravite et al, 1972).

In dissolved air flotation, air is dissolved in part of the liquid recycle from the flotation cell under 3 - 4 atm pressure. Upon reducing the pressure on air saturated liquid, very fine gas bubbles, 30 - 120 μm are generated.

This method has been found suitable for removal of oil and suspended solids from different types of waste waters (Volesky and Agathos 1974).

In electroflotation, a conducting solution is electrolysed between the cathode and anode of the electrolytic system, the current being adjusted until microbubbles which are just visible to the human eye are produced. The process has been found promising for separation of colloidal particles from dilute solutions. Lewin and Forster (1974) used electroflotation to recover proteins from dairy effluents and found that the process was economically feasible.

Being a physico-chemical process, the flotation process is affected by several chemical and physical factors. On the chemical side the role of different variables and reagents has been studied through works carried out mainly in the field of mineral flotation. The choice of surfactant, the pH of the solution and the ionic strength are amongst the most important factors.

pH of the pulp in flotation is a major factor controlling the sign and the magnitude of the charge on particles, therefore, affecting the adsorption of the surfactants and the extent of removal of particulates (suspended medium). For example, in systems where hydrogen and hydroxyl ions are the potential determining ions, e.g. quartz, oxides and silicate minerals, froth flotation employing cationic surfactants is only possible if the point of zero charge, pzc, of the particles is below the solution pH, therefore selective separation of different minerals can be achieved in practice by choosing a

proper pH (Somasundaran and Agar, 1967). pH can also influence the performance of the surfactant. For example, it is observed in some cases, around a certain pH, the collector remains in its neutral molecular form which is unable to adsorb at interfaces (Somasundaran and Fuerstenau, 1968).

Increase in ionic strength is in general known to be detrimental to froth flotation, since the adsorption of surfactant on particulates usually decreases when the concentration of counter ions competing with the surfactant is increased. The ionic strength effect is based on the fact that electrostatic adsorption of the surfactant at the interface is in competition with other ions, e.g. sulphate, calcium and magnesium ions, carrying similar charges to those of the surfactant ions. A significant increase in the concentration of these ions decrease the adsorption of the surfactant on the particle surface. It must be noted, however, that the specific adsorption properties of bivalent ions can enhance flotation when the surfactant has a charge opposite to that of these ions. The effect of ionic strength also influences the rate of flotation by affecting the distribution of potential at the interface on the solution side. An increase in the concentration of counter-ions causes a sharp decrease in the potential distribution on the surface and therefore reduces the repulsion between particle and bubble.

Increase in the flotation rate of minerals with increasing surfactant concentration has been a rather common observation. However, Reay (1973) and Collins (1975) observed that the flotation of polystyrene particles with a cationic surfactant was poor if the initial surfactant concentration was higher

than a certain limit. This behaviour was explained on the basis of the work of Connor and Ottewill (1971) on the adsorption of cationic surfactants on latex particles. That is, above a certain concentration, the surface of the particles is covered by a bilayer of surfactant molecules. The ions in the outer layer are aligned radially with their polar groups oriented outwards, thereby making the surface hydrophilic.

The physical principles of flotation have been studied comparatively less. In general, a low gas flowrate is considered to be beneficial in flotation. A relatively dry foam and high enrichment of foamate is in some cases preferable to a higher rate of separation.

The overall rate of flotation in a practical plant depends on so many factors that it is difficult to attempt a fundamental calculation of kinetics.

Different processes involved in flotation can be classified as:

- a) The introduction of feed materials into the flotation cell.
- b) The attachment of particles to bubbles.
- c) The transport processes between pulp and froth.
- d) The removal of flotation products from the cell.

Amongst the several processes involved in flotation (Trahar and Warren, 1976), attachment of particles to bubbles, which in turn involves two sub-processes, i.e. collision between particles and bubbles and adhesion of particles to bubbles, is found to be the rate determining step.

The mechanism of attachment can be described as follows.

As a bubble rises through the pulp, particles traversing along their trajectory relative to the bubble can come very close to the surface of the latter. When the gap between the particle and the bubble is small, viscous stresses within the thin film can become very high, therefore reducing the approach velocity between particle and bubble. When the film thickness decreases to less than about 1000 nm, forces of molecular origin come into play, which cause film thinning if the particle is hydrophobic. The attachment will finally occur if these intermolecular forces can overcome the high viscous forces resisting the rupture.

The final step in the process is the film recession stage in which the liquid around the point of rupture or initial coalescence between particle and bubble, draws back to form a stable contact angle with the particle surface.

To ensure continuing contact between particle and bubble in a static system, the force of adhesion generated over the finite area of contact must exceed any disruptive force associated with the weight of the particle. Also, if conditions in the flotation cell are highly turbulent, it is possible for particles to be dragged off the surface of the bubble and swept back into the liquid.

It has been shown that the smaller the particle the more difficult it is for it to detach from the bubble (Morris, 1950; Mika and Fuerstenau, 1968) so that flotation of fine particles is unlikely to be limited by their detachment from bubbles.

As several sub-processes are involved in flotation, an approach frequently employed has been to fit rate expressions to experimental data. Thus, Gaudin et al (1942) floated fine

galena particles using ethyl xanthate as the collector in a continuous system. Their results fit the following rate equation.

$$\frac{dM_c}{dt} = k M_p \quad (1.1)$$

where M_c and M_p are the mineral concentration in the concentrate and tailing stream, respectively, and k is identified with a specific flotation rate. For particle sizes between 28 and 4 μm diameter, k was found to be proportional to particle size, d_p , and independent of it for d_p below 4 μm . They found that in the presence of ethyl xanthate all particles of galena finer than 4 μm floated equally well. This was attributed to the formation of non-aerated aggregates which floated more easily than the individual particles.

As a convenient way of identifying the effect of different variables on the flotation rate constant, batch processes have been found suitable and easy to handle. Although in a batch process, the chemical and physical environment are constantly changing, the results are sound in showing the right type of dependence between the rate constant and the controlling variables in a continuous process (Trahar and Warren, 1976).

A general rate expression for a batch flotation cell can be written as

$$\frac{dc}{dt} = -kc^n \quad (1.2)$$

where c is the instantaneous concentration of particles in the cell and k and n can be obtained experimentally.

Morris (1952) fitted his data for flotation of copper pyrite

in a batch cell into a modified first order rate equation

$$\frac{dM_p}{dt} = -k(M_p - M_U) \quad (1.3)$$

where M_p is the total mass of mineral present in the pulp and M_U is an arbitrary fitting parameter. Both k and M_U were found to vary with particle size.

Bushell (1962) used expression (1.3) and specified M_U as the mass of unfloatable mineral, i.e. the amount remaining after a flotation run. In his case the rate constant did not depend on particle size but M_U/M_p was found to increase steadily with increasing size. The bubble size in both cases was not mentioned.

Tomlinson and Fleming (1963) carried out batch flotation experiments for some minerals. They found that equation (1.2) with $n = 1$ satisfactorily fitted their data. In their experiments, the rate constant was related to d_p^x . x was found to be 2 for apatite, hematite and galena and 1 for quartz for a particle size range of 20 - 200 μm . No explanation was offered for the dependence of the exponent x on the mineral species. The mean bubble size in their experiment was reported as 0.8 mm.

Somasundaran and Lin (1973) analysed a number of experimental data from the literature and fitted curves of integer order of reaction to them. They found n in equation (1.2) to vary between 1 and 2.

Reay and Ratcliff (1975) floated glass beads in the size range 4 - 20 μm and polystyrene particles of 3 - 9 μm diameter in a batch flotation cell. They found that a first order rate expression fitted their experimental data. The average

size of bubbles employed was less than 100 μm .

Collins (1975) floated polystyrene particles of 6 - 20 μm diameter in a batch flotation cell. He also found very good agreement between experimental results and a first order rate definition. The bubble size in his experiments was also lower than 100 μm .

A close examination of the previous experimental findings reveals that the commonly used approach of fitting data to rate expressions leads to conflicting results. The main reason lies in the interpretation of the rate constant, k , and the rate order, n , as recently discussed by Jameson et al (1977).

Thus, they point out that "the rate constant in flotation is not in any sense a constant, it is simply a proportionality factor that happens to apply to a particular set of conditions". They also obtained the rate equation for a batch flotation cell considering a uniform concentration of particles in the cell. Thus, taking E as the collection efficiency of a single bubble, the total number of particles removed by the bubble can be written as,

$$E \left(\frac{\pi d_b^2}{4} h \right) N_p$$

where d_b is the bubble diameter, N_p is the concentration of the particles in the cell and h is the depth of the liquid.

The rate of removal of the particles from the cell is given by

$$\frac{dN_t}{dt} = - E \left(\frac{\pi d_b^2}{4} h \right) \left(\frac{6Q}{\pi d_b^3} \right) N_p \quad (1.4)$$

where N_t is the total number of particles in the cell and Q is the volumetric gas flowrate.

Therefore,

$$\frac{dN_p}{dt} = - \left(\frac{3QE h}{2d_b V_c} \right) N_p \quad (1.5)$$

where V_c is the effective volume of the cell.

This expression indicates a first order rate of removal of particles for which the "rate constant" is

$$k = \frac{3QEh}{2d_b V_c} \quad (1.6)$$

Theoretical models proposed in the literature and summarised later in this introduction, have shown that the collection efficiency clearly varies with particle and bubble size. From equation (1.6) it is therefore evident that k can hardly, if ever, be regarded as a constant.

The effect of charge on the particle on the rate of flotation has been investigated by several workers. The maximum flotation rate for silver iodide particles (Jaycock and Ottewill, 1963) and clay particles (De Vivo and Karger, 1970) occurred when the zeta potential ($\zeta \propto$ surface potential) of the particles was zero. In both cases, coagulation could have led to growth in particle size with a consequent increase in rate constant. Also, Derjaguin and Shukakidse (1961) observed that the rate of flotation of antimonite particles dropped sharply as the zeta potential of the particles was increased beyond a critical value.

The effect of particle charge on the rate of flotation is known to result from interactions between the electrical double

layers around particle and bubble. However, very few investigators have studied the effect of both particle and bubble zeta potential on the rate of flotation. In this context, results obtained from studies of thinning of wetting films have been of special value. Blake and Kitchener (1972) following several previous studies (Read and Kitchener, 1967; 1969) on the stability of aqueous films on hydrophobic methylated silica showed that a sufficiently high repulsion could stop a contact angle from being formed on a hydrophobic surface. They demonstrated that the electrical double layer could be of particular importance in the kinetics of bubble-particle contact. They also provided an explanation for the observed fact that weakly hydrophobic solids, such as coal, can be floated faster in brine than in ordinary water.

The study of the effect of interaction of electrical double layers of particle and bubble on the flotation rate has faced considerable difficulty, mainly due to lack of reliable methods to measure the charge on bubbles. Collins et al (1978) while reviewing different methods of measuring bubble charge, presented a more reliable procedure. They measured the charge on tiny bubbles produced electrolytically in a modified electrophoresis cell. The horizontal velocity of the bubbles under an applied potential was measured as they rose up on the stationary level in the cell. Using this set up, the results were automatically corrected for the electro-osmotic streaming which was the major source of error in other available methods. Collins (1975) was able to show experimentally that the charge on both polystyrene particles and bubbles in a solution of a cationic surfactant (CTAB) was of the same sign and approximately the same magnitude. Also, in this work, the effect of the

charge on both particles and bubbles on the rate of flotation was clearly demonstrated. Thus, it was found that the rate of flotation of polystyrene particles ($d_p < 20 \mu\text{m}$) decreased sharply as the zeta potential of the particles was increased beyond a value of 45 mV (in agreement with Derjaguin and Shukakidse, 1961). The following correlation between the rate of flotation, particle size and charge on particle and bubble was put forward on the basis of the theory of coagulation of emulsions (Collins and Jameson, 1977).

$$-\ln(k/d_p^{1.5}) = 3.9 + 0.116 u_p u_b \quad (1.7)$$

where k is the flotation rate constant, min^{-1} , d_p is the particle diameter, μm , and u_p , u_b are the electromobilities of particle and bubble ($\mu\text{m/s/V/cm}$), respectively.

On the theoretical side, the first contribution to the kinetics of flotation is due to Sutherland (1948). He assumed that the rate of flotation was given by the product of three factors, namely, the rate of collision between particles and bubbles, the probability of adhesion and the probability that the adhering particles would not be subsequently detached. For particles so small as for their inertia to be neglected, and assuming inviscid flow, Sutherland proposed that collision occurred if the particle travelled on a streamline whose closest approach to the bubble surface was equal to the radius of the particle. His expression for the number of collisions per unit time is as follows.

$$N_c = 3\pi r_p r_b N_p N_b U_b \quad (1.8)$$

where r_p and r_b are the radii of particle and bubble, U_b is the

bubble velocity relative to the particles and N_p and N_b are the number of particles and bubbles per unit volume, respectively.

He defined the collision efficiency as the ratio of the number of particles colliding with the bubble to the number of particles contained within the volume swept by the bubble's cross-sectional area per unit time, i.e.

$$E_c = \frac{3\pi r_p r_b N_p N_b U_b}{\pi r_b^2 U_b N_b N_p} = \frac{3r_p}{r_b} \quad (1.9)$$

For a constant gas flowrate in the cell, the number of bubbles produced per unit time varies inversely to r_b^3 . If all the particles that collide with the bubble stick to it, Sutherland's equation predicts that the total removal rate is

$$\frac{dN_t}{dt} = \frac{Q}{\frac{4}{3}\pi r_b^3} \frac{hN_s}{U_b} = \frac{9r_p h Q}{4r_b^2} N_p \quad (1.10)$$

where $N_s = 3\pi r_p r_b N_p U_b$ is the number of collisions per bubble per unit time, and N_t is the total number of particles in the flotation cell and h is the liquid depth.

Assuming that the adhering particles do not detach from the bubble, the collection efficiency can be defined as,

$$E = E_c E_a \quad (1.11)$$

where E_a is the adhesion efficiency.

E_a is the fraction of particles which actually adhere to the bubble after collision and must be a function of the hydrodynamic and surface forces involved in the particle-bubble interaction.

Several physical factors are known to influence E_a . One

is related to the induction time which is the time required for the thin film between particle and bubble to rupture. Once collision occurs, the particle tends to slip around the bubble surface in the direction of streamlines. Unless the induction time is less than the slippage time, the particle will be swept off the bubble. Sutherland's calculation showed that particle size had no effect on the induction time, but Klassen and Mokrousov (1963) have presented experimental work to show that the larger the particle the smaller the probability of adhesion.

Another important factor affecting the adhesion is the effect of impact which becomes important when the inertia of colliding particles is not negligible. In such a case, the impact deforms the bubble surface which upon regaining its shape, causes the particle to rebound unless adhesion has occurred in the meantime.

The momentum of the particle also affects the adhesion. It has been proposed (Collins and Read, 1971) that the higher the momentum of the particle the easier it is to thin and rupture the "disjoining film", i.e. the wetting film separating bubble and particle. The lower momentum of the finer particles in a pulp could well reduce their probability of attachment to bubbles.

Difficulties in allowing for the effect of impact has made it impossible to draw a final conclusion on the evaluation of adhesion.

However, the adhesion efficiency appears to depend mainly on the chemical natures of the particle and bubble surface and on the properties of the separating liquid film. Therefore, the effect of physical variables on the overall collection

efficiency has been solely attributed to their effect on the collision efficiency.

The theory of flotation of fine particles presented by Derjaguin and Dukhin (1961) was an important step in producing a theoretical picture of particle capture mechanism in flotation. They regarded the approach of a particle to a bubble as occurring in three zones in space. In zone 1, which is a region sufficiently far from the bubble as to lie outside the range of molecular forces and diffusional processes, the particles are assumed to be acted on purely by hydrodynamic forces. The hydrodynamic drag tends to sweep the particles around the bubble, and viscous effects especially tend to retard motion between the two, while particle inertia and gravity tend to force particles towards the bubble. Zone 3 comprises the region very close to the surface of the bubble, in which forces of molecular origin predominate. In this zone of characteristic length of order of 100 to 1000 nm, the molecular forces are responsible for the thinning of the film trapped between the bubble and the particle and, eventually, for particle capture. Zone 2 was a region between zones 1 and 3 in which diffusional effects could be important. Derjaguin and Dukhin showed that a strong electric field existed in this zone due to transport of ionic surfactant to the surface of the bubble, such as occurs in any electrolyte in the presence of a concentration gradient when the cation and anion diffusivities are unequal. Charged particles in zone 2 would experience an electrophoresis force as in an electrophoresis cell and would move accordingly. The force was called a "diffusiophoretic" force. The diffusiophoretic theory predicted that below a critical particle size, and under specified conditions, attachment of particles to

bubbles would cease. The theory also predicted that the efficiency with which inertialess particles would enter zone 3 would be independent of particle size. Both of the predictions were contradicted by experimental evidence. In the first case the diffusio-phoretic theory predicts that the minimum galena particle which can be floated by 1 mm in diameter bubbles would be about 30 μm . Galena particles of 4 μm diameter were floated by Gaudin et al (1942). Meloy (1962) showed that the theory of Derjaguin predicted that all particles less than 10 μm were equally floatable. However, experimental results show a steady decrease in flotation rate with particle size, down to 1 μm (Kihlstedt, 1968; Kelsall et al, 1974).

Fonda and Herne (1957) solved the equations of motion for two spheres to find the trajectory of a particle that just grazes the surface of a collector. The collision efficiency for a sphere was then obtained by calculating the proportion of the particles that lie in front of the sphere and that actually collide with it. Both creeping and potential flow approximations were used to describe the fluid motion around the target sphere and gravitational contributions were neglected in their equations of motion. The results obtained were only applied to mist collection.

Flint and Howarth (1971) incorporated the gravitational term to the analysis of Fonda and Herne and calculated the collision efficiency for both Stokes and potential flow around the bubble as applied to froth flotation.

They found that collision efficiency depended on two dimensionless parameters, K_F and G_F , defined as

$$K_F = \frac{2\rho_p r_p^2 U}{9\mu r_b} \propto \frac{\text{inertial force on particle}}{\text{drag force on particle}} \quad (1.12)$$

$$G_F = \frac{2(\rho_p - \rho_f) r_p^2 g}{9\mu U} \propto \text{terminal settling velocity of a particle in a quiescent fluid}$$

where r_p , ρ_p are particle radius and density, and ρ_f , μ are fluid density and viscosity and r_b and U are bubble radius and its rising velocity, respectively.

Plotting the collision efficiency versus parameter K_F for different G_F , their results showed that for $K_F > 1$, i.e. large particles, the collision efficiency was strongly dependent on inertial forces and increased with increasing bubble size. For K_F less than 0.1, i.e. fine particles, they found that the collision efficiency became independent of K_F but was a strong function of G_F . In this case, the following expression was obtained for both potential and Stokes flow solutions.

$$E_c = \frac{G_F}{(1+G_F)} \quad (1.13)$$

Thus for $G_F \ll 1$, E_c becomes a function of $\frac{r_p^2}{r_b^2}$.

Flint and Howarth checked their potential flow solution experimentally. They followed the trajectory of 0.5 mm glass beads approaching nylon spheres of 12.5 mm diameter in solutions of glycerol and they found good agreement with theoretically calculated trajectories.

Reay and Ratcliff (1973) calculated the collision efficiency for systems consisting of particles of less than 20 μm diameter (typical of particle size in effluents) and bubbles of less than 100 μm diameter in the same way as Flint and Howarth. They used Stokes solution for creeping flow around a rigid sphere to describe the liquid motion around the front of the bubble and

assumed that inertial forces were negligible in the equations of motion for the particle. They obtained a simple analytical expression for the collision efficiency as a function of $\frac{r_p}{r_b}$ and $\frac{\rho_p}{\rho_f}$ only.

$$E_c = \frac{K_R^2}{(1+U_{pt})} \left[1 + U_{pt} - \frac{3}{2K_R} + \frac{1}{2K_R^3} \right] \quad (1.14)$$

where

$$K_R = 1 + \frac{r_p}{r_b} ; \quad U_{pt} = (K_R - 1)^2 (\rho_p / \rho_f - 1)$$

As a first approximation, their results provided a valuable basis for prediction of E_c dependence on bubble size and particle size.

Their theoretical results led to the following expressions for different values of ρ_p / ρ_f ,

$$E_c \propto \left(\frac{r_p}{r_b} \right)^{1.9} \quad \rho_p / \rho_f = 1.$$

$$E_c \propto \left(\frac{r_p}{r_b} \right)^{2.05} \quad \rho_p / \rho_f = 2.5.$$

To check these experimental results, Reay and Ratcliff (1975) performed batch experiments using glass beads ($\rho_p / \rho_f = 2.5$) and latex particles ($\rho_p / \rho_f = 1.05$). For glass beads of 4 to 20 μm diameter, an experimental relationship of $E_c \propto d_p^{1.5}$ was obtained. The corresponding relation for latex particles of 3 to 9 μm diameter was $E_c \propto d_p^{0.44}$. Only two experiments were performed to investigate the effect of bubble size and good agreement was found between the theoretical prediction and experimental results.

The anomalous behaviour of the latex particles was attributed to either electrical forces influencing the adhesion efficiency or to some surface chemistry effect influencing the attachment efficiency. Measurements of the charge on the particles in flotation solutions showed that the potential (ζ potential) on

the surface of glass beads was zero, while it was about + 11 mV on the polystyrene particles.

Reay and Ratcliff (1973) also calculated the collection efficiency considering Brownian diffusion as the controlling mechanism for particle transport to the surface of the bubble and obtained the following expression,

$$E \propto 1/r_b^2 r_p^{2/3}$$

Their theory also predicted a minimum in the collection efficiency around a particle size of 0.6 μm . For this marginal size, the diffusion coefficient is very low for Brownian diffusion to be the only transport mechanism to the bubble, while, on the other hand, particle inertia is very low for it to be solely subjected to the laws of hydrodynamics and be captured by the interception mechanism.

Collins (1975) has discussed in detail the similarities between the processes of flotation and deep bed filtration. For example, on the experimental side, Ives and Gregory (1966) found that double layer forces lowered the filtration efficiency. Fitzpatrick and Spielman (1973) also showed that filter coefficients dropped rapidly as the zeta potential of negatively charged particle and collector increased beyond a certain value. Similar effects were observed by Shukakidse (1961) and Collins (1975) in flotation.

On the theoretical side also, the approach that has been used to calculate collection efficiencies is similar in both processes. Spielman and Goren (1970) calculated the efficiency for a single spherical collector using the trajectory approach. In their solution, they accounted for non-retarded London/van der Waals attraction forces as well as for corrections to the drag force acting on the particles due to the presence of the

collector. They found that for small attraction forces between particle and collector, $E \propto r_p^2/r_c^2$ where r_c is the radius of the collector which is similar to the results obtained by Flint and Howarth and Reay and Ratcliff. For large values of attraction forces, the dependence was found to be $E \propto r_p^{2/3}/r_c^{4/3}$. Yao, Habibian and O'Melia (1971) incorporated Brownian motion to the analysis of Spielman and Goren and obtained $E \propto 1/r_p^{2/3} r_c^2$ for capture of submicron particles. This result is in agreement with Reay and Ratcliff's result for flotation.

Spielman and Cukor (1973) calculated the single collector efficiency for non-Brownian particles including attraction and double layer repulsion forces as well as hydrodynamic interactions between particle and collector. Their theoretical results showed a sharp decrease in efficiency for a certain value of attraction as the repulsion between particle and collector increased. This was in agreement with their experimental observations.

Another approach to calculate the single collector efficiency is that of Prieve and Ruckenstein (1974). They calculated the efficiency of a collector by integrating the flux of particles over the collector surface which results from the combined effects of diffusion and convection transport mechanisms. They included gravity and attraction forces as well as hydrodynamic interactions between particle and collector.

Collins (1975) calculated the collection efficiency of neutrally buoyant particles approaching a bubble. His solution is based on that of Prieve and Ruckenstein. Improvements introduced in this theory over those of Flint and Howarth and Reay and Ratcliff are,

a) London/van der Waals attraction forces are included in the

analysis.

b) Hydrodynamic corrections due to the presence of bubble are introduced to calculate the drag force on the particle. The corrections are those applicable to a small particle approaching a much larger collector surface (i.e. the latter is regarded as planar). Collins' results for collision efficiency by a bubble of about 100 μm in diameter and particles in the size range 6 - 20 μm is

$$E \propto \frac{r_p^{1.3}}{r_b^2}$$

The weaker dependence between collision efficiency and particle radius as compared with the results of Reay and Ratcliff can be attributed, of course, to the effect of attractive force and introduction of hydrodynamic corrections to the transport equations. Collins' experimental results with polystyrene particles showed a dependence of $E \propto r_p^{1.5}$. Also Fitzpatrick and Spielman (1973) found that the filter coefficient in their experiments was proportional to dp^x where x was 1 - 1.5. For strong repulsion between particles and collectors, x was 3. These results are in fair agreement with the above mentioned theory.

Collins also calculated collection efficiencies in the limiting case of purely Brownian motion. He obtained $E \propto \frac{1}{r_b^2 r_p^{2/3}}$ in agreement with Reay and Ratcliff (1973).

A study of capture efficiency of small particles by single bubbles was conducted by Anfruns and Kitchener (1977). Single bubbles were produced at the bottom of a column and allowed to rise through a dilute solution. The experiments were carried out with quartz and spherical glass beads, 10 - 50 μm in diameter. The bubble size was varied between 0.5 and 1.1 mm.

The same authors also proposed a theoretical model to compare with their experimental results. On the same lines as Reay and Ratcliff (1973), they calculated the collision efficiency on the basis of hydrodynamic and gravity forces alone. As their bubbles were large, a solution at $Re = 40$ for flow around the front of the bubble was employed. Their theory predicted that the collision efficiency was approximately proportional to d_p^2 . The dependence of E_c on bubble size was found to be $E_c \propto d_b^{-1.3}$ for particles between 27 and 40 μm .

The correspondence between the theory and the experimental results obtained for spherical glass beads was very poor. In some cases the collection was only 20% of the calculated collision rate. However, the results for quartz particles were in good agreement with their theory. As the surface properties of both types of particle were assumed to be identical, the high collection efficiency of quartz was attributed to its roughness.

On the other hand, the poor efficiency of collection of spherical particles was thought to be due to the action of surface forces. The existence of a strong potential energy barrier opposing particle-bubble contact in the case of methylated silica in distilled water had been already observed (Blake and Kitchener, 1972). To check on the effect of electrical repulsion forces, a concentration of 1M of KCl was added to the solution. This concentration was sufficient to cancel electrical double layer repulsion between surfaces, thereby increasing the collection efficiency by a factor of 3 as compared with that in distilled water. As the results were still much lower than the theoretical prediction, discrepancies were attributed to the time required for the viscous film trapped between the surfaces of the particle and the bubble to

thin and rupture. A rough estimation for a bead of diameter 32 μm indicated that this time was substantially larger than the average contact time between the particle and a bubble of 0.6 mm diameter.

Fukui and Yuu (1980) have recently measured the total collection efficiency in a flotation cell containing suspensions of submicron polystyrene particles of average size 0.6 μm in diameter. H_2 bubbles 20 μm in average diameter were produced electrolytically and their charges as well as those of the particles were also measured.

These authors calculated single bubble collection efficiencies by solving the diffusion equation and integrating the flux of particles over the bubble surface. Their theory incorporated non-retarded London/van der Waals attraction and electrical double layer forces.

As in their experiments the concentration of bubbles was low, comparison of data with theory was possible and good agreement was obtained. However, the bubble rising velocity used in their theoretical analysis is supposedly wrongly experimentally measured. Thus, a value of 1 cm/sec is reported for a bubble of 20 μm in diameter. Therefore, agreement between theory and experiment must be regarded as doubtful (Yuu et al, 1977).

The study undertaken in the present work concentrates on the removal of emulsified oil particles from effluents using dispersed air flotation.

In Chapter 2, a brief review of the present state of knowledge on the process of oil flotation as well as the specific aims of the experimental part of this thesis are outlined. The work carried out is then described and the chapter closes with a discussion of the main findings.

In Chapter 3, the theoretical approach employed to calculate collision efficiency for a single bubble is presented. Different theoretical models, as given by previous authors, are briefly reviewed in the introduction to the chapter, and the direction of the present work is outlined. Calculation of hydrodynamic interactions as well as intermolecular forces between two spheres are given in separate sections. In the last section, the equations of motion for two arbitrarily moving particle and bubble are given, followed by determination of grazing trajectory leading to calculation of the collision efficiency.

In Chapter 4, the dependence between the overall rate of flotation obtained experimentally and the particle and the bubble size is discussed. The relation between the single bubble efficiency to the particle and the bubble size is also determined theoretically. Comparisons are then made between these results as well as to other applicable theoretical models.

2.1 Introduction

Oil-containing wastewaters from refineries and many other sources like petrochemical, food and paint industries, often require supplemental treatment of standard oil-water separator effluents in order to reduce remaining oil to acceptable levels.

In practice, a gravity type oil-water separator is normally used for primary treatment to separate large oil droplets from wastewaters. This technique becomes impractical as the size of the particles diminishes.

Flotation as a secondary treatment of waste water has proved to be a potential process in handling dilute solutions (normally less than 1000 ppm) of emulsified oil particles (around 1 μm in diameter), by reducing their initial concentration to 15 ppm or lower.

Up to now, dissolved air flotation has been most widely used in oil effluent treatments. This process is normally accompanied by a flocculation stage prior to flotation and basically involves pressurizing and dissolving air into a recycle stream consisting of 20 - 50% of the clarified effluent stream flow. Upon releasing the pressure on the air saturated liquid, small bubbles are precipitated in the flotation chamber which attach themselves to the dispersed particles.

Rohlich (1954) carried out a thorough examination of the process, experimentally. He studied the effect of air to water recycle ratios on the efficiency of the process and found that the efficiency was maximum at a certain air concentration and decreased as the concentration of dissolved air

increased. He also examined the effect of flocculents and found that addition of 25 ppm alum increased the efficiency by 15 - 23%.

Several pilot studies have been carried out upon the effect of pH, type of flocculant and its dosage on the efficiency of this process. Volesky and Agathos (1974) summarise some of these results.

In general, a pH of 6 - 8.5 and a dosage of 20 - 70 ppm of aluminium, ferric salts or 100 ppm of lime have been found to be the most effective. The amount of oil removed from waste waters under such circumstances has been reported between 80 - 95%.

Organic surface active agents have also been used as coagulants in dissolved air flotation. Luthy et al (1978) have recently conducted pilot plant studies on the removal of emulsified oil from refinery wastewaters using different organic coagulants.

They employed several commercial anionic, cationic and nonionic surfactants in their experiments and obtained a high amount of oil removal (98%) with 15 ppm dosage of a cationic surfactant. They also found that with alum the optimum removal was achieved at a concentration of 25 ppm but the efficiency was always lower than that obtained with the cationic surfactant.

The other interesting result from this investigation was that the effluent oil concentration from the flotation plant was not directly dependent on the influent oil concentration and

some of the highest influent oil concentration yielded some of the lowest effluent oil concentration. This observation is in line with the results of Roth et al (1960), who found that the oil removal efficiency in pilot plant tests on refinery wastes decreased from 97% to 80 - 85% and 65 - 70% as the oil input concentration decreased from 150 ppm to 100 ppm and 25 ppm respectively. They also found that the effluent oil concentration did not increase significantly when the influent water conductivity was increased from 4000 $\mu\text{mhos/cm}$ to 9000 $\mu\text{mhos/cm}$ through the addition of sodium chloride.

Theoretical modelling of the process has received considerably less attention, as it would require a thorough examination of the particle and bubble behaviour.

The process of attachment of oil droplets to bubbles is normally complicated by the fact that upon release of pressure in dissolved air flotation process, the air bubbles may either form on the surfaces of the droplets or in the bulk water with subsequent interception and capture of the droplets.

Assuming that bubble nucleation on oil droplet surfaces is insignificant as compared with interception between bubble and droplet, Luthy et al (1978) used the simple hydrodynamic model of Reay and Ratcliff and applied it to dissolved air flotation of oil particles. Their results showed that the rate of oil removal is directly proportional to r_p^2 and inversely proportional to r_b for a given gas hold-up. In other words, the oil droplets should be large and the air bubbles small for good process performance.

Russian workers have lately carried out some investigations

on the flotation of emulsified oil using dispersed air flotation in batch systems. Their method to produce the bubbles consists of passing air through a glass porous plate fitted at the base of a column, 4 - 5 cm in diameter.

Skrylev and Artemova (1974) studied the floatability of oil droplets in emulsions of industrial oil in distilled water. 250 ml of emulsion were processed using an air flowrate of 2 - 4 lt min⁻¹. Their experiments were carried out with or without surfactants. Several types of surfactant, including cationics (e.g. a mixture of primary amines, amine acetates, etc.) and anionics (e.g. alkyl carbonates, alkyl sulphates, etc.) and a cationic-anionic (gelatin) were used. Only the cationic surfactants and the cationic-anionic (gelatin) were found to increase the efficiency of flotation above that obtained without the aid of surfactants. The increase in the recovery was attributed to the adsorption of the collector (surfactant) on the surface of the droplets with consequent reduction of the negative surface charge to almost zero.

Skrylov, Savina and Sviridov (1975) studied the effect of different cationic surfactants on the flotation of emulsified vegetable oil. Several quaternary pyridinium and quinolinium salts containing n-alkyl chains of different length were used. 50 ml of the emulsion of oil in distilled water were floated using an air flowrate of 700 - 800 cm³ min⁻¹. The initial concentration of oil was between 100 - 150 ppm and the particle size was in the range of 1 - 10 µm.

Their results showed that the efficiency increased as the length of the hydrocarbon chain increased from C₇ to C₁₁ and dropped for chain lengths larger than C₁₃.

After measuring the electromobility of the particles for different surfactants, they concluded that those compounds with longer hydrocarbon chain lengths tended to stabilise the emulsion while the ones with shorter chains caused coalescence of the droplets due to a decrease in the magnitude of the charge on the oil particles. The concentration of the surfactants used was varied between 1 - 5 ppm.

Skrylev, Ososkov and Pochtarenko (1975) studied the effect of particle size on the overall efficiency using emulsions of industrial oil in distilled water. The initial concentration of oil varied between 250 - 400 ppm and the size of the particles, which were negatively charged, varied between 0.5 - 5.0 μm . The amount of emulsion treated was 500 ml and the air flowrate was adjusted at 120 $\text{cm}^3 \text{min}^{-1}$. This study showed that the flotation efficiency dropped as the particle size decreased from 5 μm to 0.5 μm . A mixture of primary aliphatic amine salts as well as an amine acetate were used as collectors.

Skrylev et al (1976) floated emulsions of different industrial oils in distilled water in order to study the effect of stabilisers on the removal efficiency. 300 ml of emulsion with particle sizes in the range 0.5 - 8 μm were treated. Of the different stabilisers used, a cationic (laurylamine) outperformed the anionic and nonionic types. They explained their findings by suggesting that the air bubble-water interface was negatively charged. Next, they used some surfactants as collectors in order to float the particles which were already stabilised by a stabiliser. Their results showed that the best performance was achieved when a cationic surfactant (rosine

amine acetate) was used as collector in emulsions stabilised by anionics and nonionics, or vice versa. In their experiments, the nature of the oil had no significant influence on its separation.

Sviridov et al (1977) floated oil emulsions arising in waste waters from the coal-chemical industry with the same type of cationic surfactants and experimental set up as used by Skrylev et al (1975) for flotation of emulsified vegetable oils. The size of the oil particles was in the range of 2.5 - 5 μm . The results on the effect of different surfactants on efficiency had the same tendency as was observed by Skrylev et al.

In some of these experiments, an overall efficiency of up to 95% was obtained. Best efficiencies were normally achieved when the magnitude of charge on the particles was low or, in other words, when coalescence was likely to happen. In fact, the maximum efficiency in flotation of emulsified vegetable oil dropped from 93% to 40% when hydrocarbon chain in quaternary pyridinium chlorides increased from C_{10} to C_{16} . This was attributed to the higher surface activity of the higher homologs of the pyridinium salts which would have led rather to stabilisation than to coalescence of the droplets.

The bubble size was not reported in any one of these works. However, it has been found (Kalman, 1974; Kaufmann, 1974) that to produce small bubbles on a glass frit, a frother which is normally a short chain aliphatic alcohol must be used in concentrations of 0.1 - 0.5 V/V.

The lack of a single economical method for separation of oil from water has been discussed by Wang et al (1975). Problems

arising from the necessity of pressurising the water, large space required for pressure retention tank, as well as a flocculation stage prior to flotation, have rendered the dissolved air flotation process to some extent unattractive.

In this work, a study was undertaken to investigate the performance of dispersed air flotation for handling emulsions of minute oil droplets ($d_p < 10 \mu\text{m}$) in water.

In order to have a well-defined system with which to carry out fundamental investigations into the mechanisms of the oil flotation, emulsions of oil in distilled water were prepared with different amounts of salts in solution. Tap water was also used in some preliminary experiments.

Although a steady state continuous system approximates more closely the real conditions in a flotation plant, this type of set up was avoided mainly due to considerable volume of emulsion required for each run. Batch systems are easy to handle and have proved to be suitable for studies on kinetics and on the effect of different variables involved in the flotation process.

A simple device was made to produce small gas bubbles.

In order to study the effect of particle size on the rate of flotation, stability of the oil particles in the emulsions was controlled through the addition of a surfactant.

2.2 Experiments and Techniques

In this section details of the experimental work and different techniques used to analyse the results are described.

Series of batch flotation experiments were conducted in a flotation cell of 6 litres capacity.

The bubbles were produced by means of a modified venturi device and measured by a photographic technique.

A surfactant was used as both frother and stabiliser.

Samples taken during runs were analysed for particle concentration and size distribution to provide information on flotation kinetics. These measurements were carried out by means of a Coulter Counter apparatus.

2.2.1 Flotation Apparatus

A schematic view of the apparatus employed in this work is shown in Figure 2.1.

The flotation unit consisted of a glass cylindrical column (1), 85 cm high and 9.5 cm in diameter, provided with connections for air inlet, liquid recycle and foam removal.

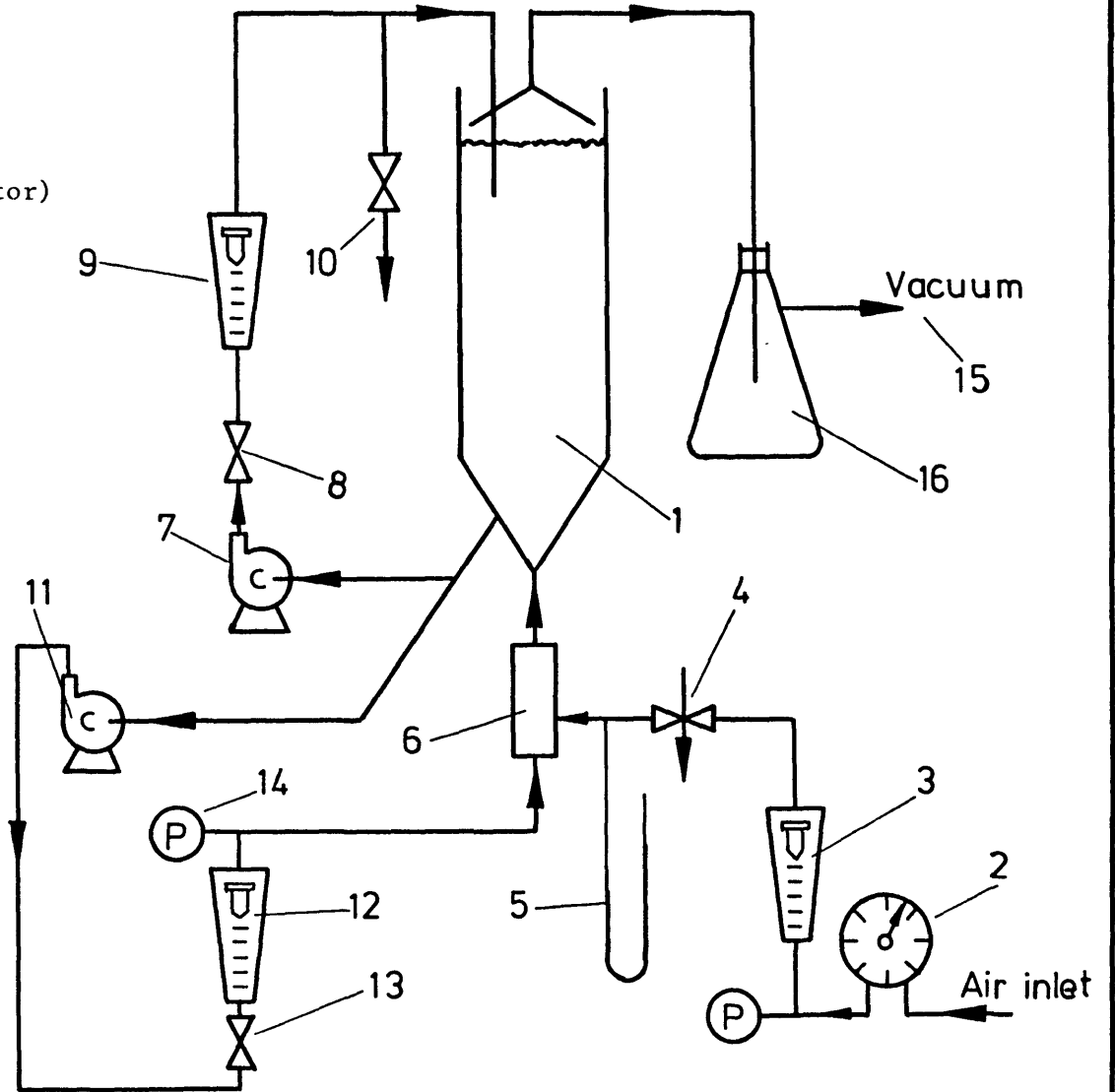
Air was first passed through a wet gas flowmeter (2) (Alexander Wright & Co., 0.25 dm³/rev); next, a rotameter (3) and an Edwards high vacuum needle valve (4) were used to monitor and adjust the gas flowrate respectively. A mercury manometer (5) was also installed in this line to measure the gas pressure in the suction line at the bubble generation device inlet (6).

Part of the liquid extracted at the bottom of the column was recycled to the top of the flotation column by means of a low pressure centrifugal pump (7) (TEP pump, Model 175 B/M/DP) and the resulting flowrate was measured through a rotameter (9).

This recycle was used for two purposes; namely, to ensure that

FIGURE 2.1: Schematic diagram of the experimental set-up

1. Flotation column
2. Wet gas flowmeter
3. Air rotameter
4. Needle valve (gas flow regulator)
5. Mercury manometer
6. Bubble generation device
7. Low pressure pump
8. Liquid flow regulation valve
9. Liquid rotameter
10. Sampling valve
11. High pressure pump
12. Liquid rotameter
13. Liquid flow regulation valve- 14. Liquid pressure meter
- 15. Vacuum pump
- 16. Foam flask



the samples taken from the column through (10) at different time intervals were truly representative of the actual liquid composition in the column, as well as to provide stirring both prior and during an experimental run.

The rest of the liquid extracted from the bottom of the flotation unit was sent into the bubble generation device (6) by means of a high pressure centrifugal pump (11) (Stuart Turner Ltd., 1.5 - 6.1 Hm, 9.1 - 3 l/min). Liquid flow rate measurements and regulation were provided by rotameter (12) and valve (13). A manometer (14) (Fisher, 0 - 2 Kg/cm²) was also installed to measure the upstream liquid pressure of the venturi.

The foam accumulated at the top of the column during a run was continuously sucked into a waste flask (16) by means of a high vacuum pump (Edwards High Vacuum Ltd., single stage model) connected at (15).

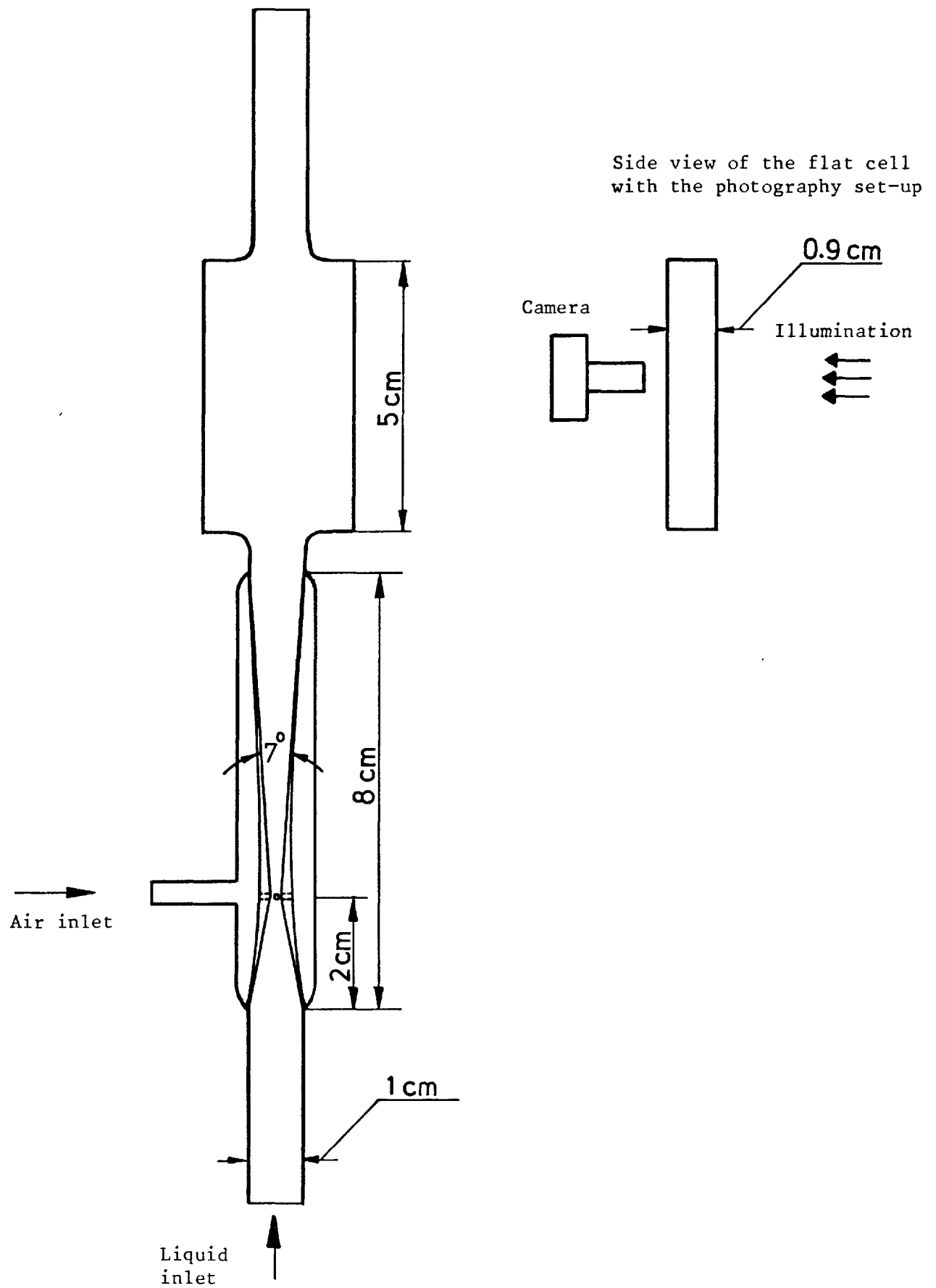
2.2.2 Bubble Generation Device

An enlarged sketch of the bubble generation device (6) shown in Figure 2.1 is presented in Figure 2.2. The top part consists of a rectangular cell which enables photography of the generated bubbles for subsequent size distribution measurements.

The lower portion, the bubble production section, is basically a modified venturi type of device. For this particular application small holes, 0.4 to 1.0 mm in diameter, are drilled along the throat perimeter. The throat itself has a diameter in the order of 1 to 2 mm.

When the velocity of the liquid at the throat is adequate, i.e. above 10 m/s, air is sucked in through the holes due to the vacuum produced. The relation among the different parameters, such as upstream liquid pressure, throat pressure and liquid flow rate, cannot be analysed on the basis of classical formulae applying to venturi

FIGURE 2.2: Bubble generation device (front view)



tube meters. Therefore, the performance of such a device has to be found experimentally.

The effect of upstream liquid pressure as well as pressure in the suction line on the amount of entrained gas was studied. Some results obtained for different systems investigated during the flotation experiments are shown in Figures 2.3, 2.4 and 2.5. Figures 2.6 and 2.7 illustrate the effect of those same parameters on bubble size.

Different venturries were also designed to analyse the effect of throat and orifice size on the performance of the systems. A summary of the specifications for the various venturis used is given in Table 2.1.

TABLE 2.1: Specifications for different venturis studied

	Approx dia of throat mm	number of holes	approx dia of hole mm	upstream liquid pressure bar	air flowrate fully open valve cm ³ /min	liquid flowrate ℓ/min
1	1.88	2	1	0.5	307	2.83
2	1.94	2	0.8	0.5	230	2.93
3	1.6	2	0.4	0.5	98	2
4	1	3	0.6	0.55	66	0.75
5	2.05	3	0.5	0.4	390	3.41

As it can be observed, a wide range of gas flowrates is obtained depending on both the diameters of throat and holes. The values reported in Table 2.1 correspond to the case where the needle valve is fully opened and the upstream liquid pressure is close to the maximum

FIGURE 2.3: Effect of vacuum in the suction line on the amount of gas entrained, upstream liquid pressure = 0.5 atm.

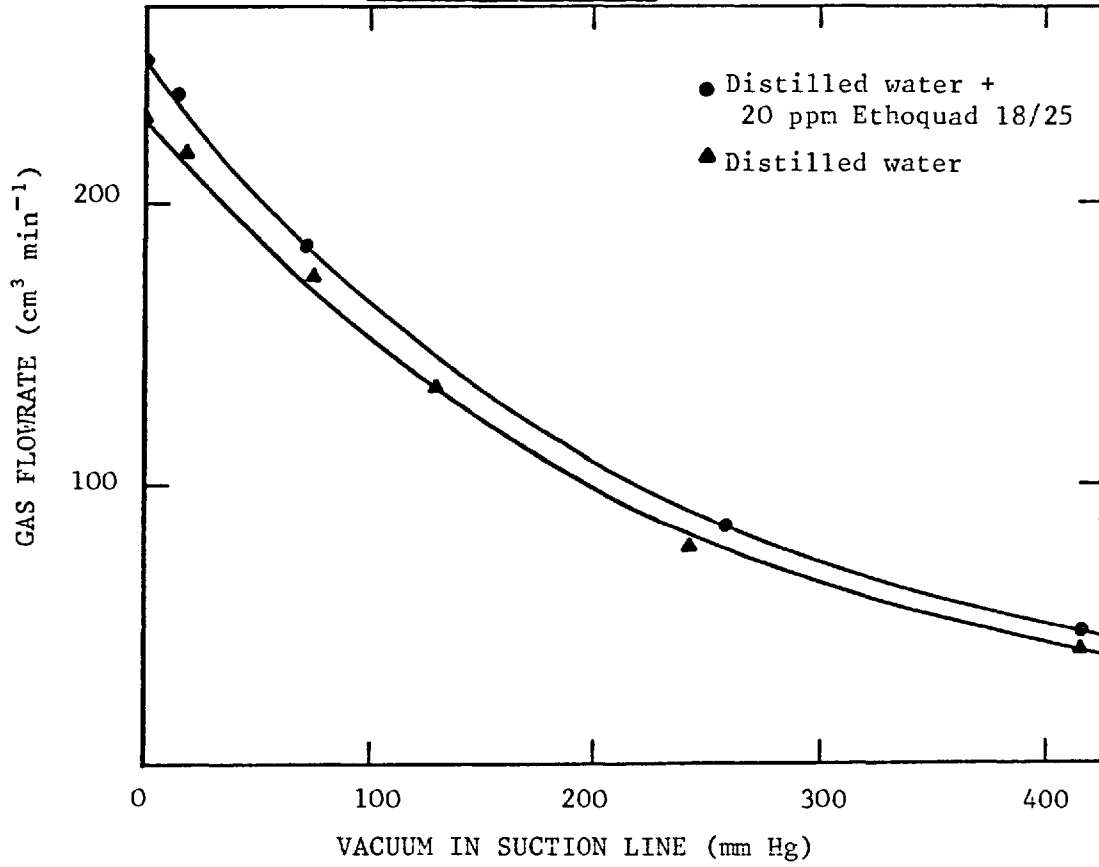


FIGURE 2.4: Effect of upstream liquid pressure on the amount of gas entrained, the needle valve fully open

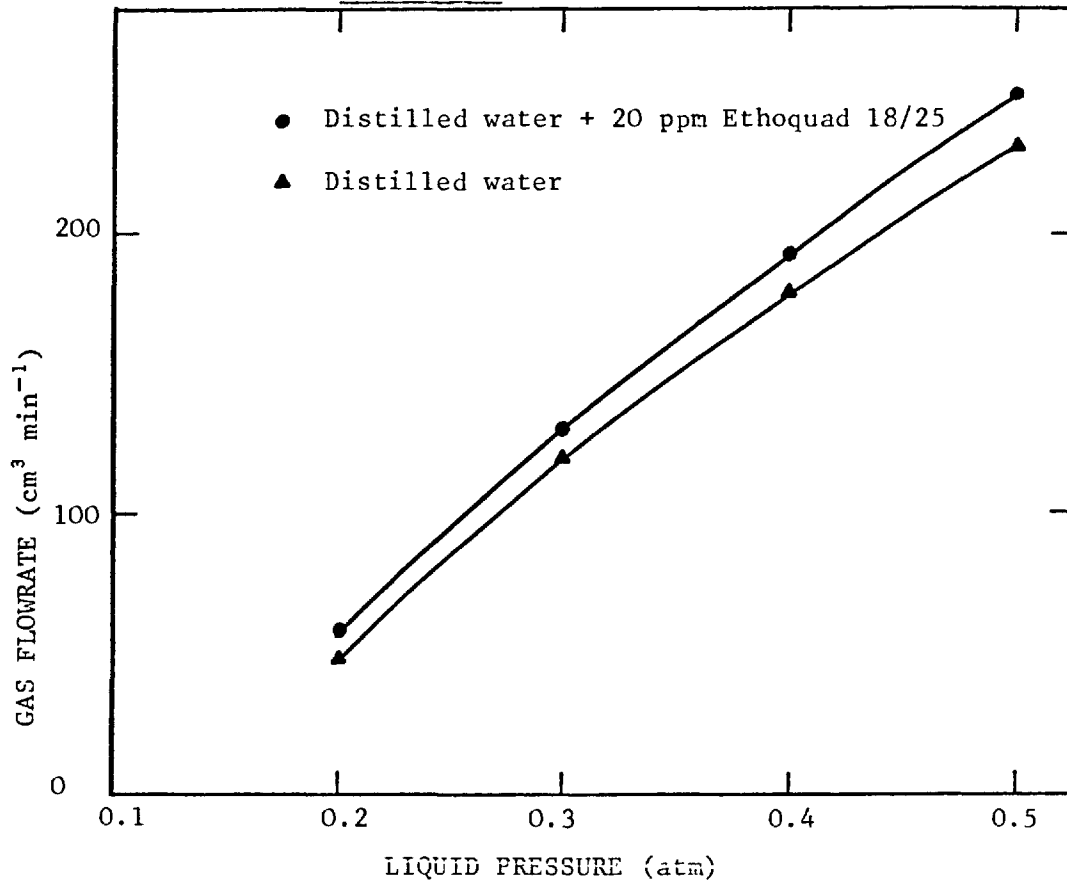


FIGURE 2.5: Effect of vacuum in suction line on the amount of gas entrained for different liquid pressures, tap water + 20 ppm Ethoquad 18/25

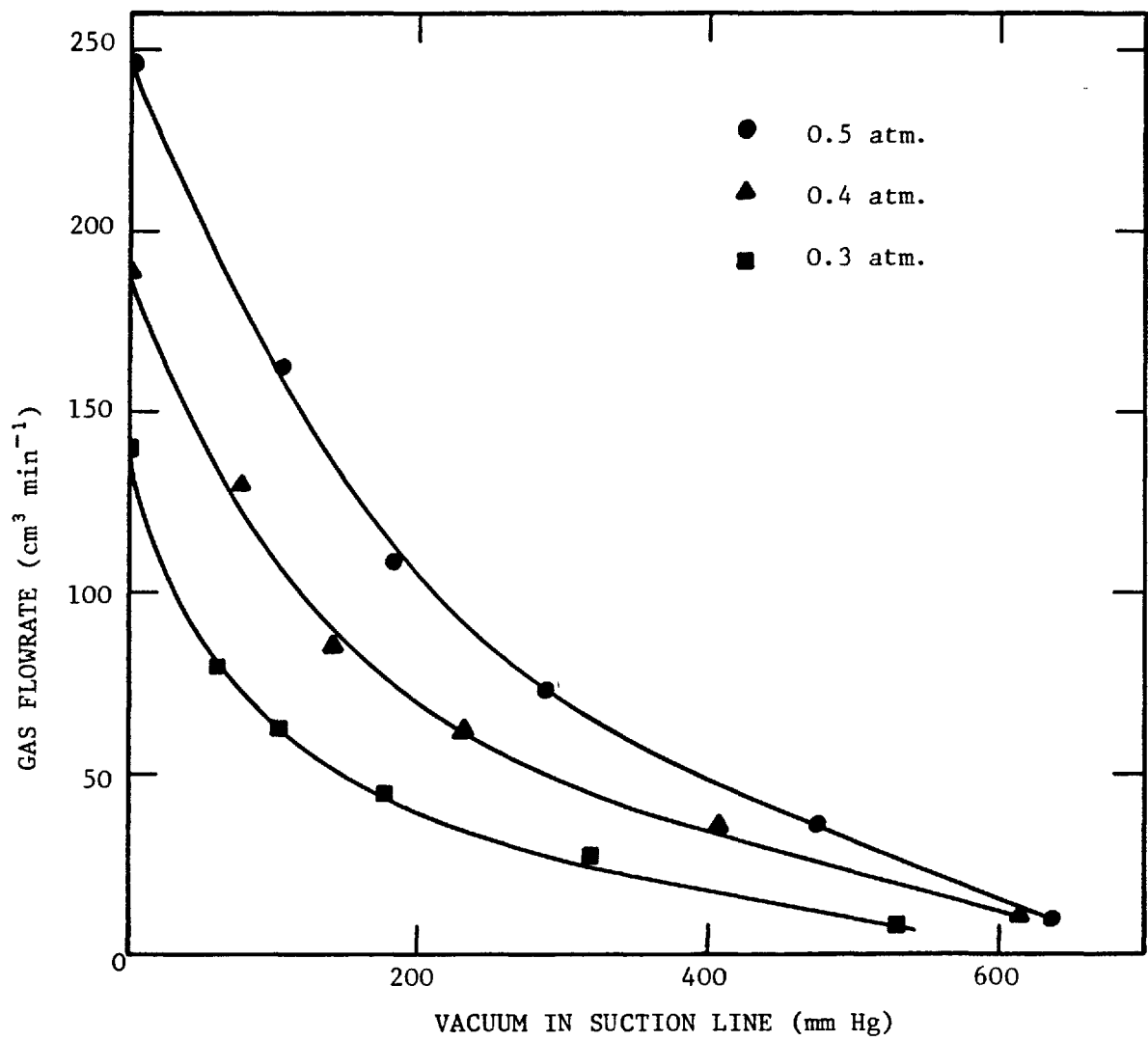


FIGURE 2.6: Effect of vacuum in suction line on bubble size,
liquid pressure 0.5 atm

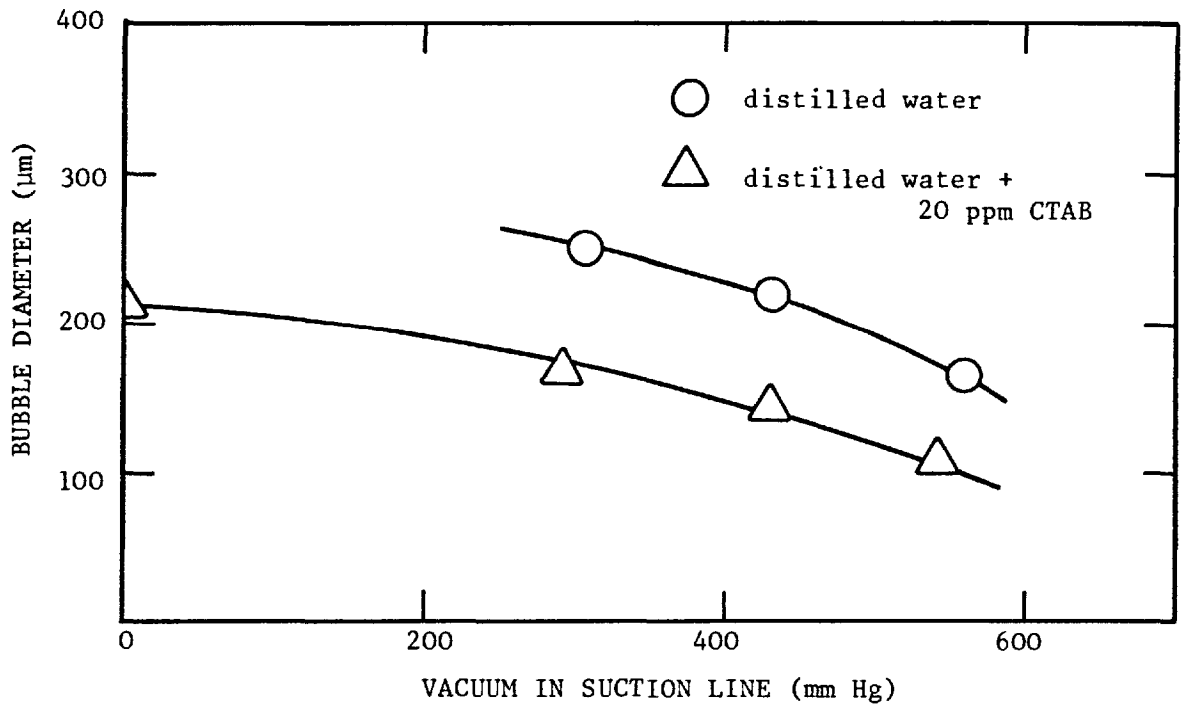
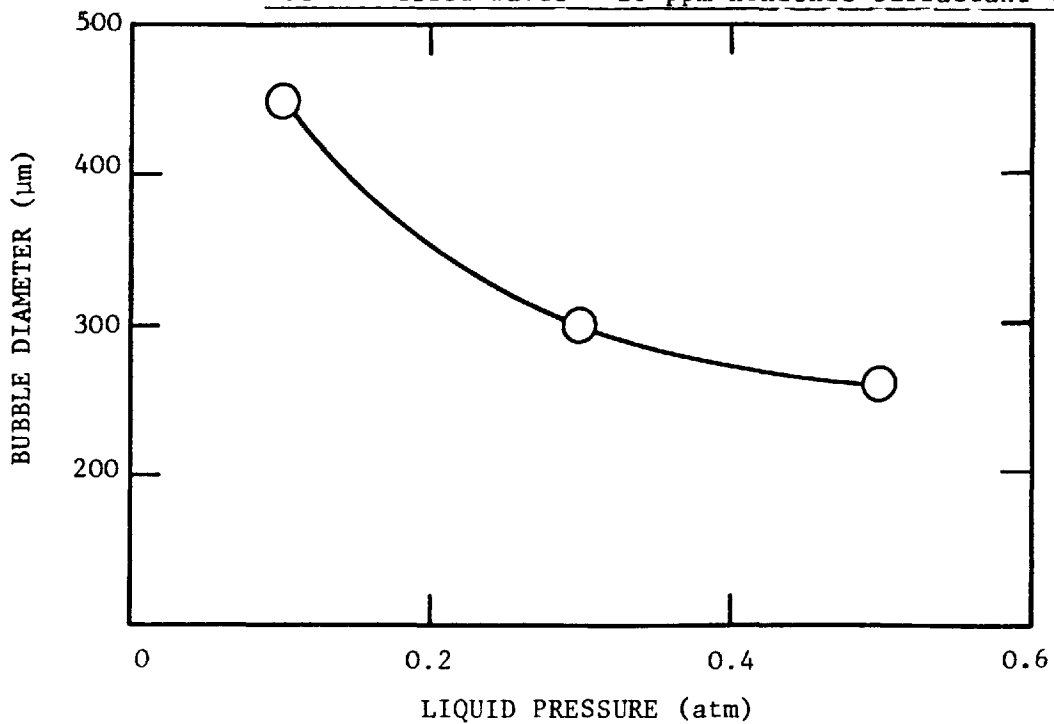


FIGURE 2.7: Effect of upstream liquid pressure on bubble size
for distilled water + 20 ppm nonionic surfactant (Nonidet
P-42)



pressure provided by the pump.

In general, an increase in the cross sectional area of the throat results in a larger gas flowrate, due to an increase in the liquid velocity. This becomes evident on comparing the performances of venturis 4 and 5. Larger air flowrates are also obtained by increasing the diameter of the holes. This latter effect can be observed upon comparing the behaviour of venturis 1 and 2.

Thus, depending on the range of gas flowrate required for the flotation experiments, a suitable venturi can be chosen.

In general, those venturis with a larger throat offer a wider range of gas flowrates. However, they have the disadvantage of increasing the turbulence in the system due to the higher liquid flowrates involved.

To analyse the interactive role of the different variables and the effect of throat size on these variables, two of the venturis can be compared. Thus, assume that an air flowrate of 200 cc/min is required for a flotation column. Several alternatives can be suggested to provide this flow, and Table 2.2 lists four, employing two different venturis.

Consider cases 2 and 4, for which the needle valve is fully open (no vacuum in the suction line). Higher liquid flowrates, as previously pointed out, are obtained, with the venturi having a larger throat (case 4). On the other hand, the upstream liquid pressure, which is a measure of the energy consumption of the system, is lower for this case.

Also a comparison between cases 1 and 3 shows that the liquid flowrate is higher for the latter. However, in case 3, the higher vacuum produced assists the generation of smaller sized bubbles, which was confirmed photographically.

Although comparison between these two venturis at different

upstream pressures might seem rather crude, it should be pointed out that an increase in the upstream pressure (e.g. to 0.5 atm for case 3) would further increase the liquid flowrate and the vacuum in the suction line to produce the same gas flowrate.

TABLE 2.2: Performance of two of the venturis studied (constant gas flowrate)

	Approx dia of throat mm	upstream liquid pressure bar	vacuum in the suction line mm Hg	gas flowrate cm ³ /min	liquid flowrate ℓ/min
1	1.94	0.50	33	200	3.04
2	1.94	0.44	0	200	2.75
3	2.05	0.40	66	200	3.69
4	2.05	0.31	0	200	3.04

Summarising, the observations of the behaviour of the bubble generation device clearly show that

- a) for a certain device, higher vacuum in the suction line would produce a reduction in the bubble size;
 - b) an increase in the upstream liquid pressure would provide smaller bubbles;
- ((a) and (b) were both confirmed by photographic evidence)
- c) an increase in the area of the throat, for the same gas flowrate, would cause an increase in the liquid flowrate (more turbulence), a decrease in the upstream liquid pressure (less energy consumption), an increase in the vacuum in the suction line (smaller bubble size).

Therefore, to obtain a suitable range of gas flowrates together with an adequate bubble size within a certain flotation column, the

key variables mentioned above have to be optimised.

For most of the flotation experiments in this work, device No. 2 was used, although in some of the preliminary experiments, No. 1 was also used. The suitable set of variables was obtained mostly on the basis of photographic examination and observations of the extent of turbulence in the column.

2.3 Materials

2.3.1 Water

The water used in the flotation experiments was single distilled as obtained from a commercial pyrex apparatus. It had a conductivity of 5×10^{-8} mho/cm and a surface tension of 72.46 dynes/cm at 25°C. It was therefore used without further treatment.

2.3.2 Oil

The oil used was BDH analytical reagent grade n-decane. Before use, it was treated to remove polar compounds by passing through a column 1 cm in diameter and 1 m long. The lower half was packed with 100 - 200 mesh chromatographic grade silica gel (Hopkin and Williams) and the upper half with activated alumina (CAMAG, M.F.C. neutral, Hopkin and Williams). Purity was checked through surface tension measurements by the maximum force on a ring, at 24 ± 0.5 °C. A value of 52.0 dynes/cm was obtained which was in excellent agreement with that of 52.03 dynes/cm reported in the literature (Johnson and Dettre, 1966).

2.3.3 Salts

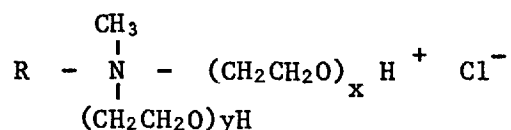
All the salts used were BDH analytical reagent grade materials except for NaCl which was purchased as a general laboratory reagent. The salts were used without further purification.

2.3.4 Surfactants

Different types of surfactants were employed during this work. In most cases they were industrial grade materials and, unless otherwise stated, were used as supplied.

Cetyl trimethyl ammonium bromide (CTAB), a cationic surfactant, was used during the preliminary experiments. This was a BDH product of analytical reagent grade quality.

Two other surfactants, commercially known as Ethoquads (kindly donated by AKZO Chemie, UK) were also used. Ethoquads are basically polyethoxylated quaternary ammonium salts with the following general chemical structure



where R represents an alkyl chain derived from a fatty acid. The molecule can be rendered less cationic by increasing the number of ethylene oxide groups.

Two products within this family were used in the flotation experiments, namely, Ethoquad 18/12 with two ethylene oxide groups ($x + y = 2$), and Ethoquad 18/25 with fifteen ethylene oxide groups. The alkyl chain in both derives from stearic acid.

Information provided by the manufacturer on both surfactants indicated an activity of 75% for Ethoquad 18/12, the impurities consisting mainly of solvent isopropanol and about 2% of free amines. As regards the 18/25 product, the activity is reported as 95% with, again, as much as 2% content of amines.

Ethoquad 18/12 was purified by five times recrystallisation from acetone and water. Attempts to purify the 18/25 surfactant by either recrystallisation or vacuum distillation were, however, unsuccessful. Both products were analysed by gas chromatography. It was found that the impurities content was not significant (refer

FIGURE 2.8: Gas chromatography analysis of impure sample of Ethoquad 18/12

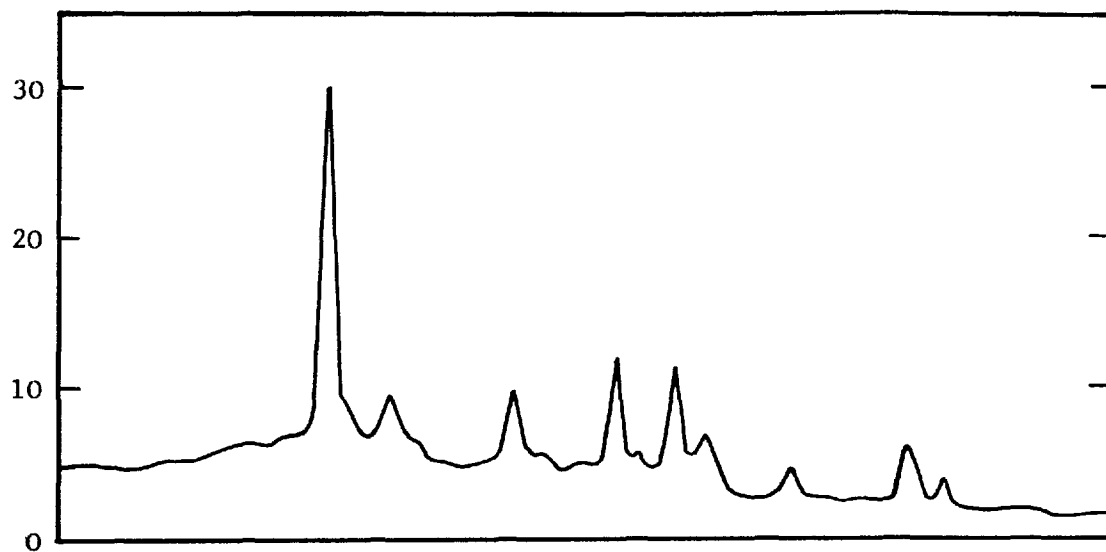


FIGURE 2.9: Gas chromatography analysis of purified sample of Ethoquad 18/12

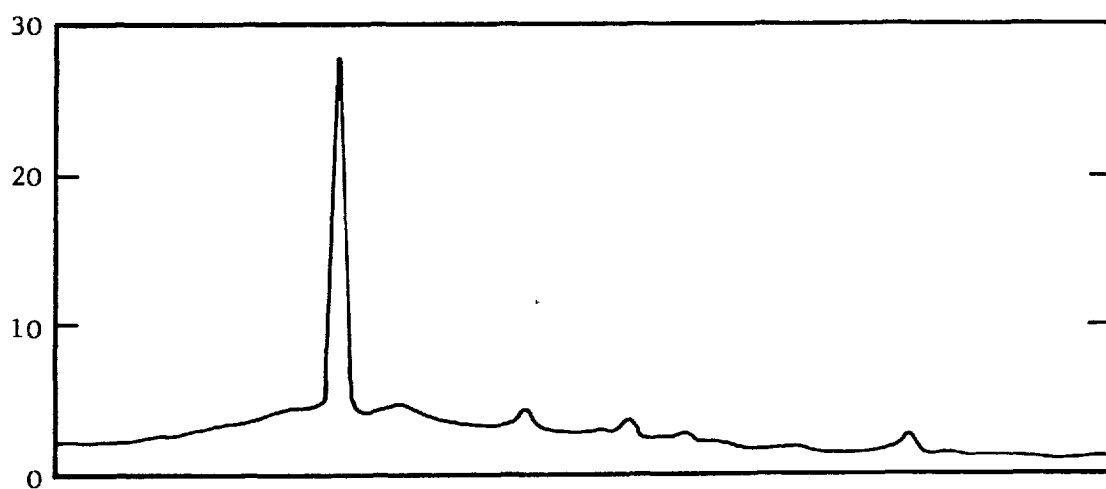
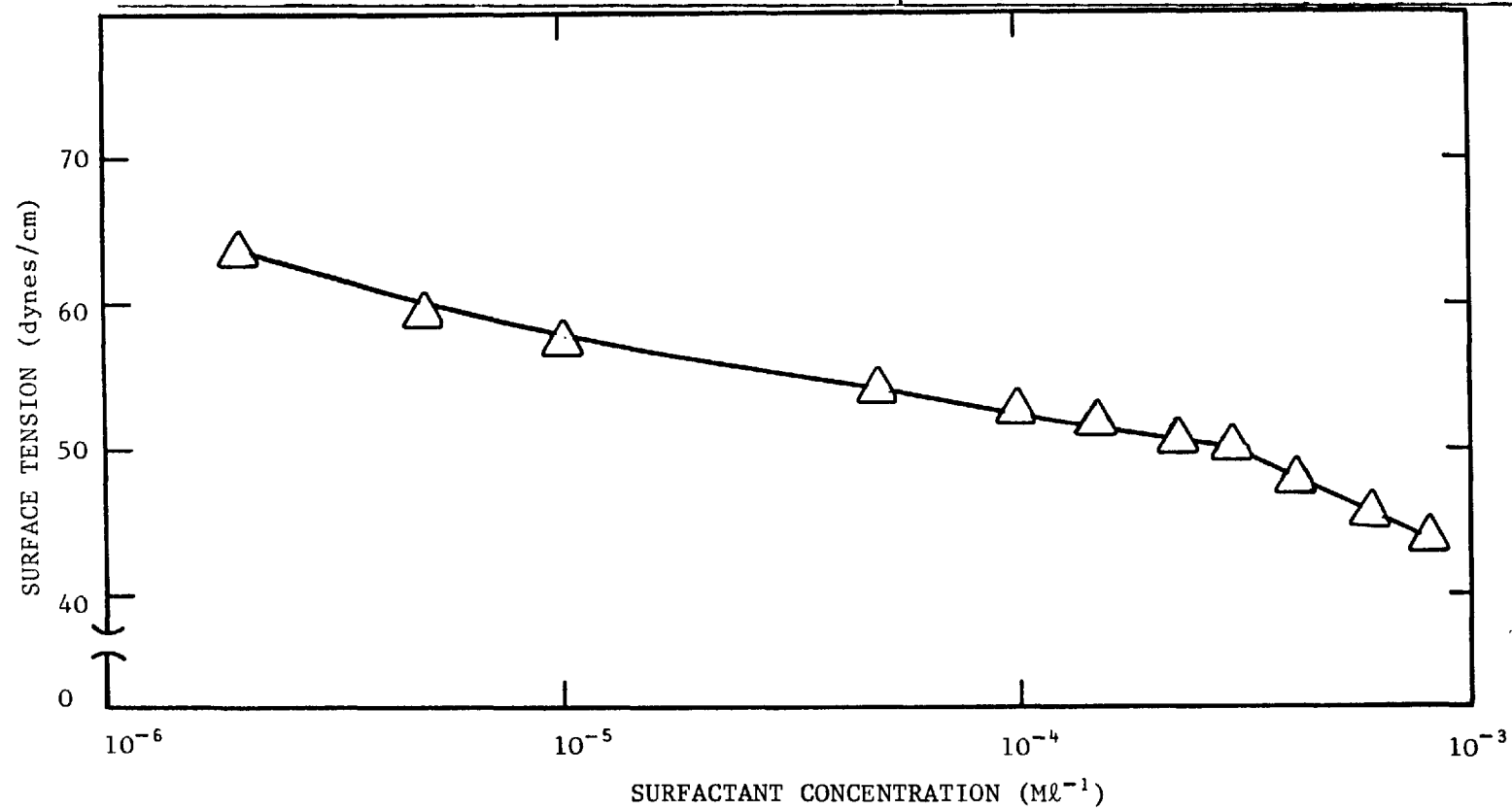


FIGURE 2.10: Gas chromatography analysis of impure sample of Ethoquad 18/25



FIGURE 2.11: Surface tension of solutions of Ethoquad 18/25 in distilled water vs. concentration



to Figures 2.8, 2.9 and 2.10).

Measurement of surface tension for various concentrations of Ethoquad 18/25 was also carried out. The results are shown in Figure 2.11. A continuous decrease in surface tension for increasing concentration of surfactant is observed. Absence of a minimum in the curve suggests the absence of impurities exhibiting higher surface activity than the main surfactant. It was therefore decided to use this product as supplied.

2.4 Preparation of the Emulsion

Several methods were tried to prepare the emulsion of oil in water. Most of these, however, failed to produce the required type of emulsion, i.e. with a narrow range of size distribution (1 - 10 μm).

A summary of the different techniques tried is given in Appendix 1.

2.5 ml of oil in 1.25 - 1.5 litres of water was used for each run throughout the trials. The amount of the surface active material used was kept between 5 - 10 ppm.

Amongst the different techniques tried, a modified ultrasonic homogeniser offered the most effective way to produce a suitable emulsion.

2.4.1 Ultrasonic Homogeniser

Use of sonic and ultrasonic energy to disperse one immiscible liquid into another has been studied for many years (Sherman, 1968).

To prepare the emulsion, a small batch ultrasonic homogeniser (Minisonic Model 4, Ultrasonic Ltd.) was used. The principal of operation of the system is simple. The mixture to be processed passes through a nozzle, and the high speed jet produced in this way

impinges on a blade which, as a result, vibrates at its resonant ultrasonic frequency. An extremely high level of cavitational energy is therefore generated and used to process the mixture. Cavities produced through the propagation of the ultrasonic waves subsequently collapse, and upon their collapsing extremely powerful shock waves are produced which in turn are responsible for most of the effect on the processed product.

Those parts of the system in direct contact with the mixture (e.g. the pump, the vibrating element, etc.) were made out of stainless steel, and the apparatus was able to handle quantities up to two litres.

2.4.2 Modified Ultrasonic Homogeniser

Amongst the different techniques to produce a suitable emulsion, one of the best ways was found to be as follows. A small teflon tubing, 3 mm in diameter, was connected to a 5 ml burette, and both were placed inside one of the containers of an ultrasonic emulsifier with the teflon tubing bent towards the inlet to the pump.

To make the emulsion the container in which the burette was placed was filled with water (1.5 litres). Once the system was switched on and adjusted (pump pressure 160 - 170 psi), the oil was allowed in at a very low flowrate and the resulting emulsion was discharged into the second container equipped with a stirrer. The emulsion was allowed to recycle three to four times through the system, depending on the amount of unemulsified oil left in the mixture. It was finally discharged into a separate vessel where it was stirred rather close to the surface for 2 minutes.

The emulsion obtained in this way was reasonably good, with fewer particles below 1 μm , marginally bigger sizes of particles and with more homogeneous distribution than the ones tried before.

2.5 Bubble Size Measurement

In order to obtain the bubble size distribution, a flat cell was incorporated into the system to enable photography of the bubbles.

Out of several designs tried, a $0.9 \times 2.1 \times 5.0$ cm rectangular cell was found to be the most suitable. Other designs tried are given in Appendix 2.

Photographs taken from the middle part and sides of the photography cell showed that the bubbles were distributed almost homogeneously across the cell.

An Exakta Varex IIa camera (Zeiss Biotar, 58 mm f/2 lens) with its bellows attachment was used. This system was placed on a support in front of the cell. Illumination was by back-light, provided by a flash (power consumption 50 joules/flash) covered with a sheet of tracing paper which acted as a diffusing screen. The shutter speed of the camera was fixed at 1/25 sec and an f8 aperture was found to be the best for the type of arrangement used.

The film used was fine-grain black and white Kodak Panatomic-X, ASA 32.

A piece of transparent scale was placed on the side of the cell whenever photographs were to be taken. The procedure was such that the camera was first focused on the scale and a photograph was taken at this position. The set up was then moved parallel to the scale and was placed right in front of the cell. Assuming that the bubbles which were on the same focal plane as the scale would appear the sharpest in the photographs, only those bubbles which were rather well in focus were therefore measured.

To measure the bubbles, the photographs were analysed with a X-Y digital reading analyser (P.C.D. Ltd.). A total magnification of $\times 47$ was obtained from the bubbles to the analyser screen.

The results from the analyser were obtained on punched paper tapes, and these were later processed to calculate the mean bubble

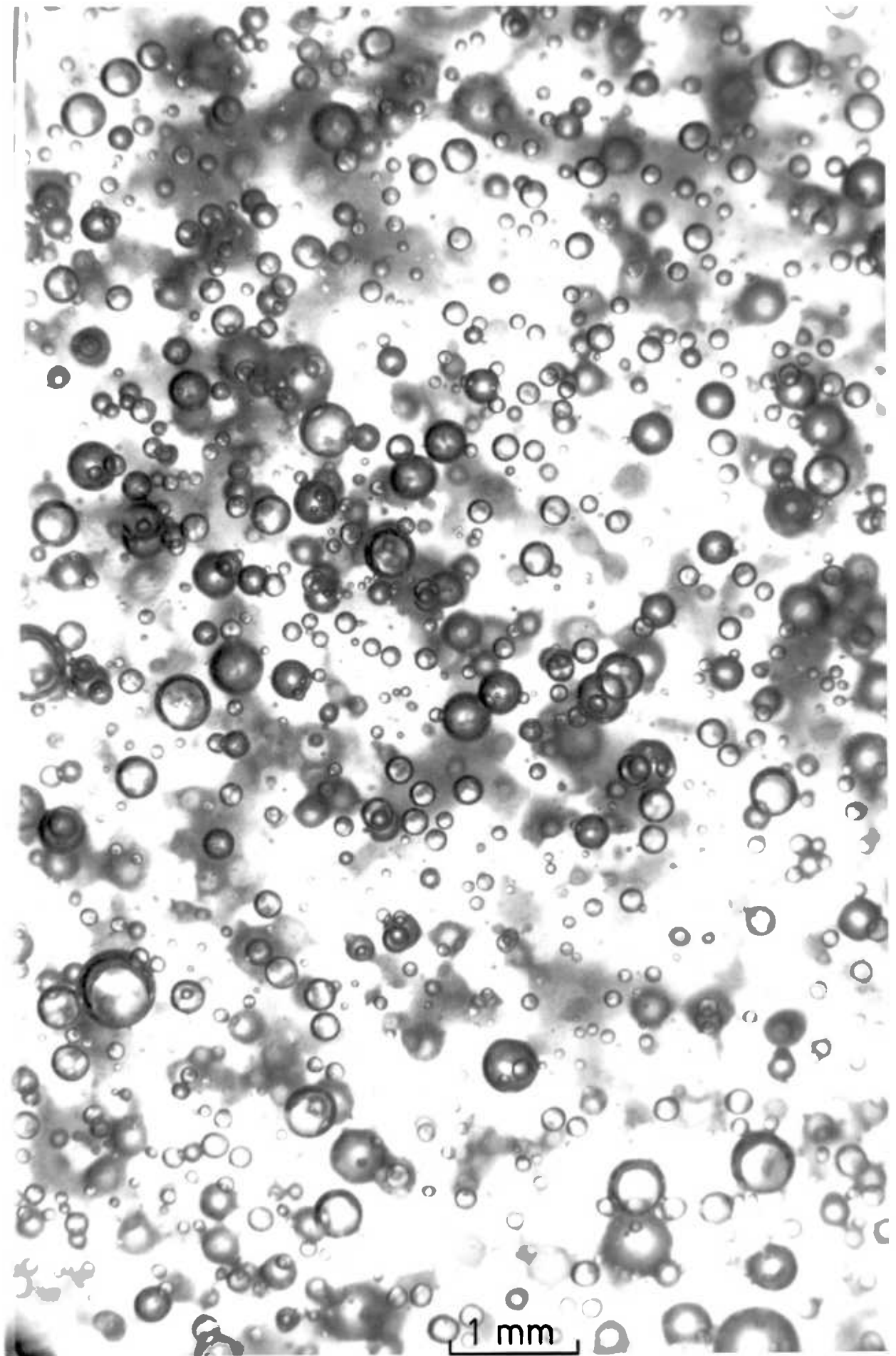


FIGURE 2.12 _ Photograph of Bubbles

FIGURE 2.13: Bubble size distribution in the flotation column. Salt concentration $10^{-1}\text{M Na}_2\text{SO}_4$, surfactant concentration 20 ppm Ethoquad 18/25, pH = 9.1

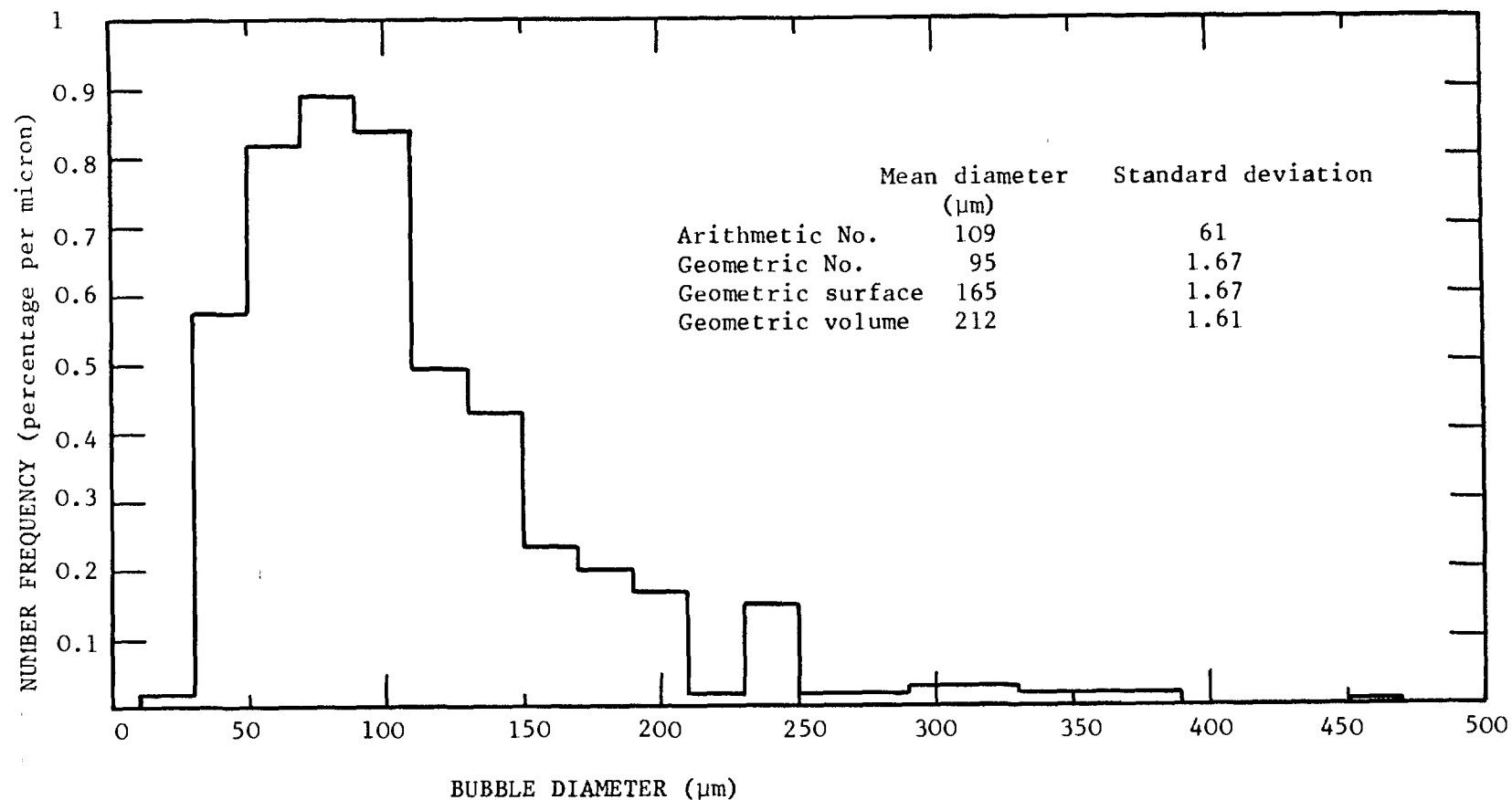
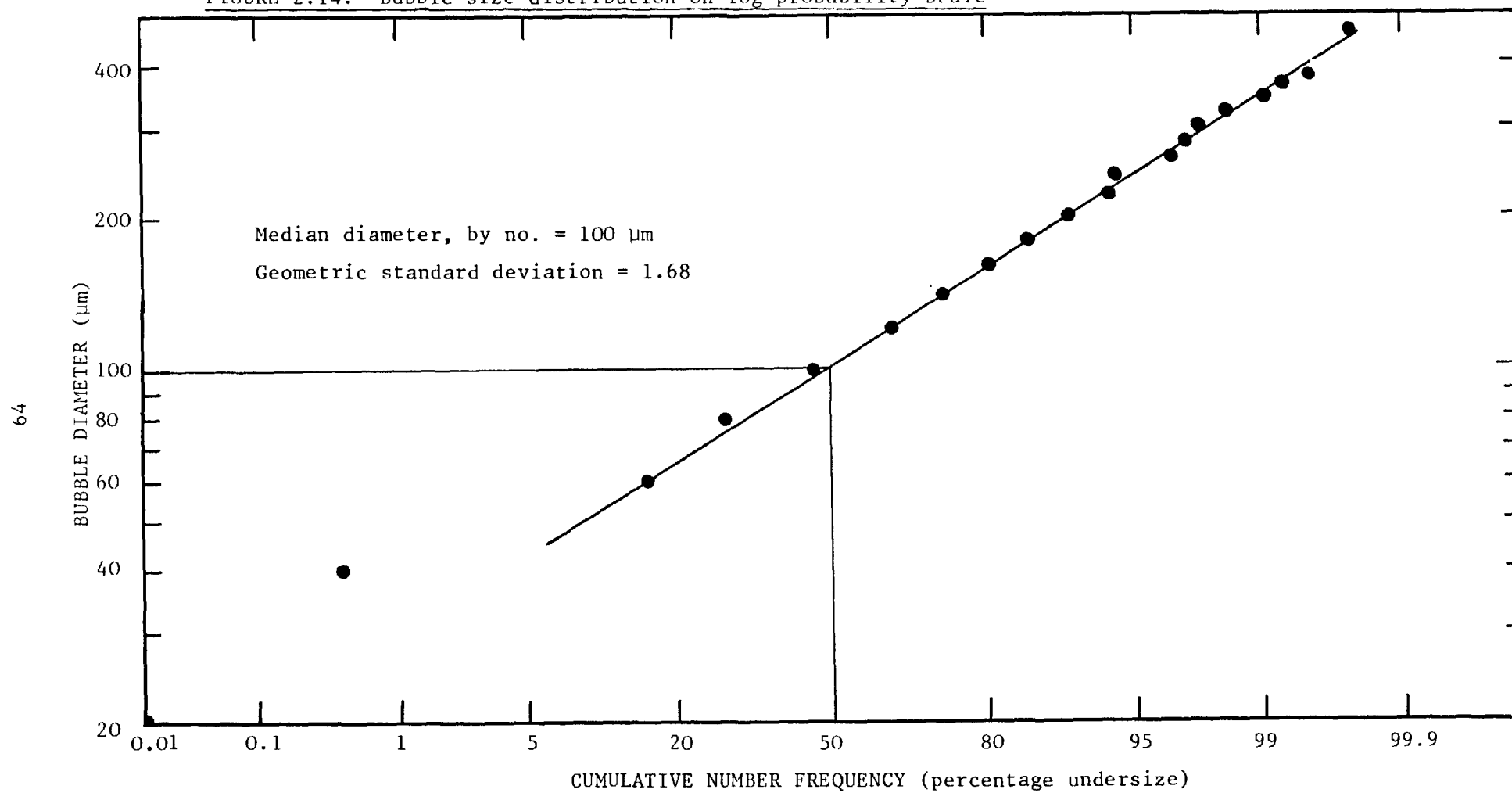


FIGURE 2.14: Bubble size distribution on log-probability scale



size.

A program (PROGRAM BUBBLE) was written to convert these data into mean sizes. This program calculates various mean sizes with their standard deviations. A photograph of the bubbles is shown in Figure 2.12.

The skewed shape of distribution in Figure 2.13 shows that the bubble size distribution is far from obeying a normal distribution. When plotted on a log-probability paper, a straight line is obtained (Figure 2.14), therefore indicating that the distribution obeys a log normal law.

On the whole, the measurement of the bubbles was rather a tedious job; in particular, as the bubbles showed a diffused pattern in some of the photographs, finding the exact border of the bubble proved rather difficult.

2.6 Particle Size Measurement

As a preliminary, the particle size distribution was measured by microscopy. Most of the particles were found to be between 0.5 - 8 μm .

As coalescence of the particles is an inevitable process, a fast and accurate method for measuring a large number of particles is therefore essential. Several methods were considered, which are briefly summarised here.

2.6.1 Microscopy

This method is probably the most tedious one for measuring the particles. Photographs taken from a sample under a microscope were analysed by an analyser (refer to Section 2.5). A total of 500

particles were measured to obtain an accurate measure of size distribution.

As in the case of this work, a knowledge of the number of particles was essential, therefore microscopy could not be applied. It was used only as a check to compare the results obtained with another technique, to be described later.

2.6.2 Light Scattering

This method has been shown to be an accurate way of measuring particles of up to 2 μm in diameter. Unfortunately, it could not be used in this case, as there were many particles above 2 μm and the multi-scattering due to the larger particles was expected to disturb particle measurement.

2.6.3 Coulter Counter

The Coulter Counter is found to be a suitable device for size distribution analysis of emulsions (Shotton and Davis, 1968; Walstra and Oortwijn, 1969).

The Coulter Counter basically determines the number and size of the particles suspended in an electrically conductive liquid. The suspension is forced to flow through a small aperture having an immersed electrode on either side.

As a particle passes through the aperture, it changes the resistance between the electrodes. This produces a voltage pulse of short duration having a magnitude proportional to particle size. The series of pulses is then electronically scaled and counted.

The pulse height and instrument response are essentially proportional to particle volume, and to fluid resistivity.

A series of counts at selected threshold levels provide the adequate data for particle size measurement.

An electrolyte must be used as the suspending medium. Therefore,

the dilute sample must be checked for absence of aggregation, due to the high electrolyte concentration required for this method.

Provided several other precautions are taken, such as against dust and acoustic noises, particles down to $0.6\text{ }\mu\text{m}$ can be counted and sized. Those below this limit can be accounted for by means of suitable extrapolation techniques (Coulter Counter Handbook, 1973).

The reproducibility of results obtained by this method is good and a high accuracy can be achieved as the instrument is capable of counting a large number of particles.

A Coulter Counter Model Z_B (Industrial) with a $50\text{ }\mu\text{m}$ orifice tube was used throughout this work.

A solution of 0.9% Na Cl, filtered through $0.22\text{ }\mu\text{m}$ Millipore filters was found to be suitable as the suspending medium. All glassware required was cleaned by first washing with detergent and tap water, then rinsing with distilled water and finally drying in an oven at 130°C . This procedure proved satisfactory as the count for the filtered solution, at the most critical setting of the apparatus, was found to be lower than the limit recommended by the manufacturer.

To observe the effect of the electrolyte on the stability of the emulsion particle, counts were repeatedly determined over fifteen minutes, i.e. the average time required for the complete analysis of a sample. No obvious change in particle counts was observed and it was concluded that no aggregation had taken place.

During the measurements, the apparatus stirrer was not used, as it was observed that stirring produced tiny bubbles which tended to upset the readings.

The instrument was placed in a dust and noise free environment to minimise sources of error.

2.6.3a Calibration of the Instrument

A 50 μm orifice tube was used for all measurements. The resistance of the aperture was determined according to the instructions manual and a value of 24 $\text{K}\Omega$ was obtained. The matching switch of the system was therefore set at 20 $\text{K}\Omega$.

The apparatus was calibrated against particles of known size, supplied by Coulter Counter Electronics. Two different samples were used, namely, a polystyrene DVB latex of 9.09 μm and a DVB latex of 3.15 μm diameter. The calibration factor, based on an average of four determinations, was found to be 1.0724.

2.6.3b Measurement of Particle Size Distribution

Figure 2.15 shows a photograph of a typical sample of the emulsion as observed through a microscope (Carl Zeiss Jena Ltd.) and Figures 2.16 and 2.17 show the distribution of the particles.

Due to the limitation of the instrument for sizes below 1 μm , a suitable extrapolation technique was used to check on the contribution of particles in this range of sizes to the cumulative volume. Figure 2.18 shows that this contribution is negligible. Therefore, in most of the experiments the lower average limit for particle counts was set at 1 μm .

In Figure 2.17 the particle diameter is plotted versus the cumulative volume frequency on a log probability paper. It clearly shows that the emulsion obeys a log normal distribution of particle size as reported by other authors in the literature (Shotton and Davis, 1968).

To define an average size for the distribution, a geometric volume mean diameter was regarded as the most suitable parameter to represent a mean of the distribution, as particle analysis was done by Coulter Counter.

FIGURE 2.15: Photomicrograph of oil particles

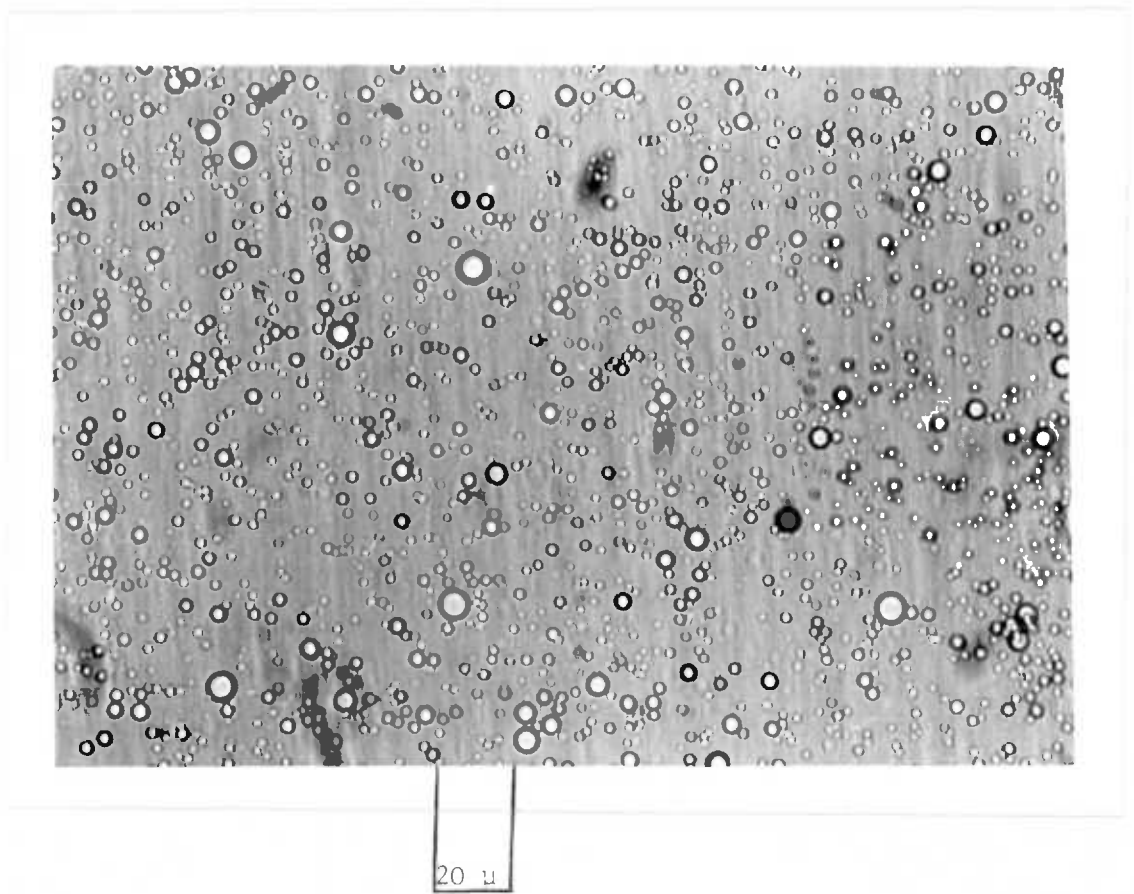


FIGURE 2.16: Particle size distribution in the flotation column

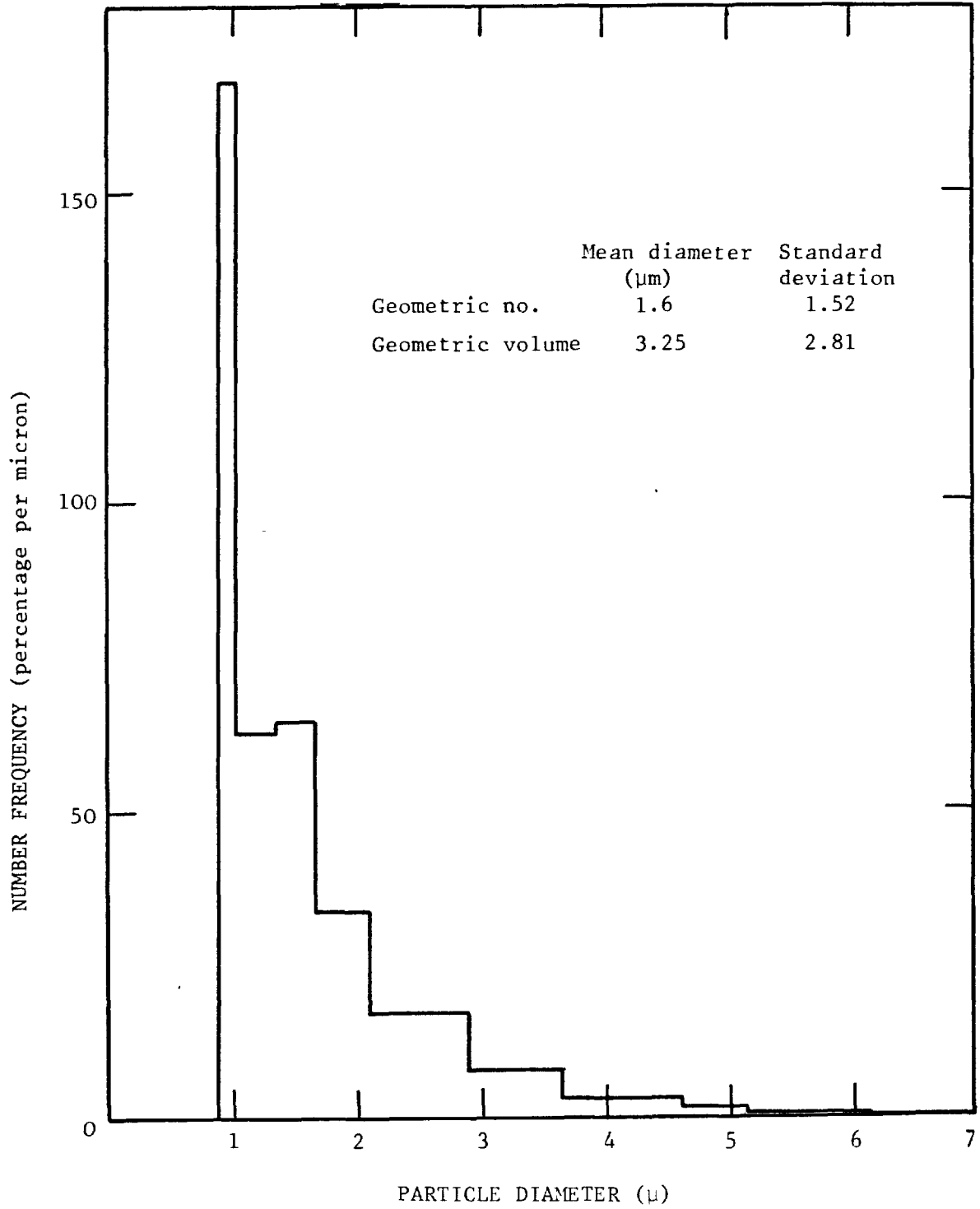


FIGURE 2.17: Particle size distribution on log-probability scale

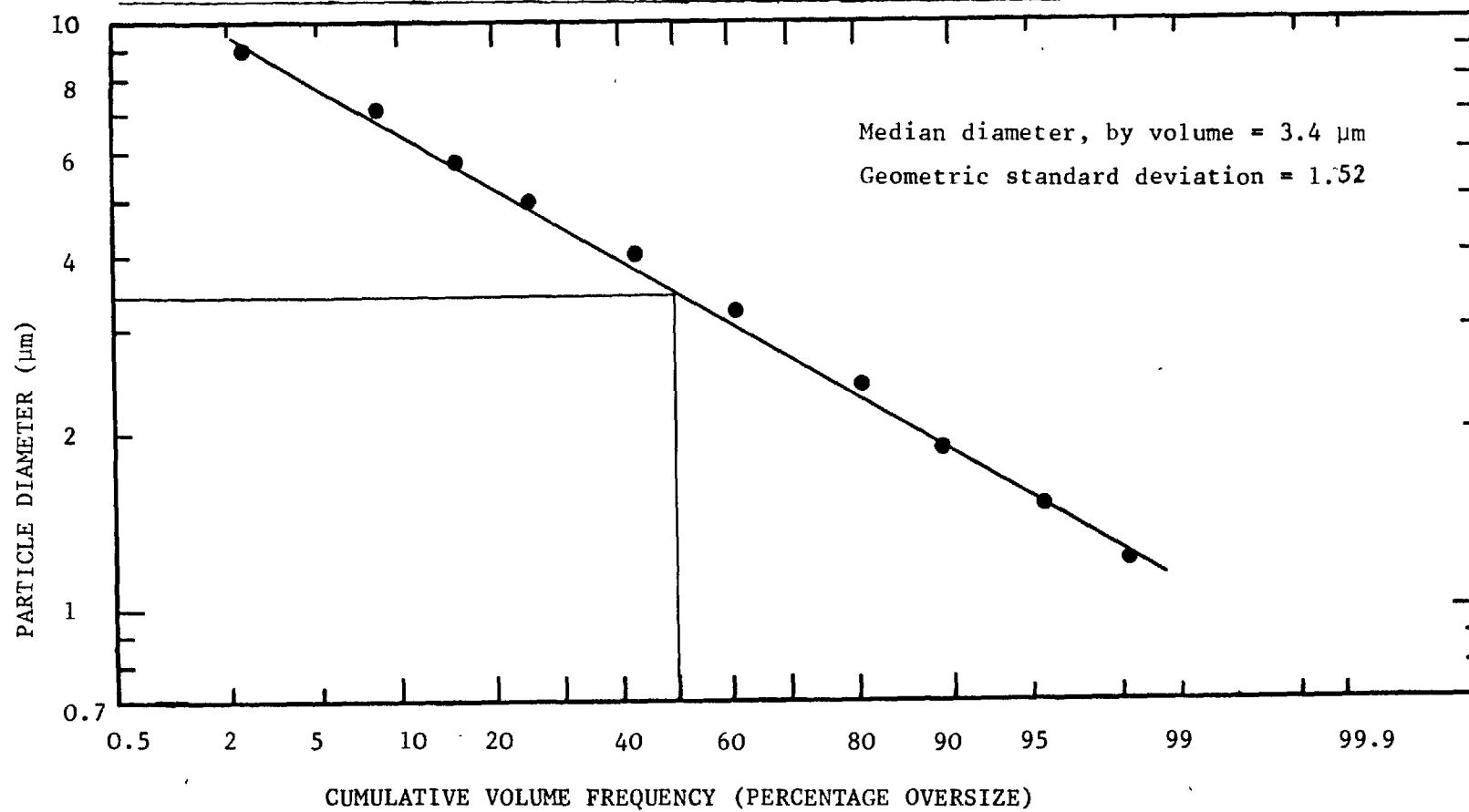
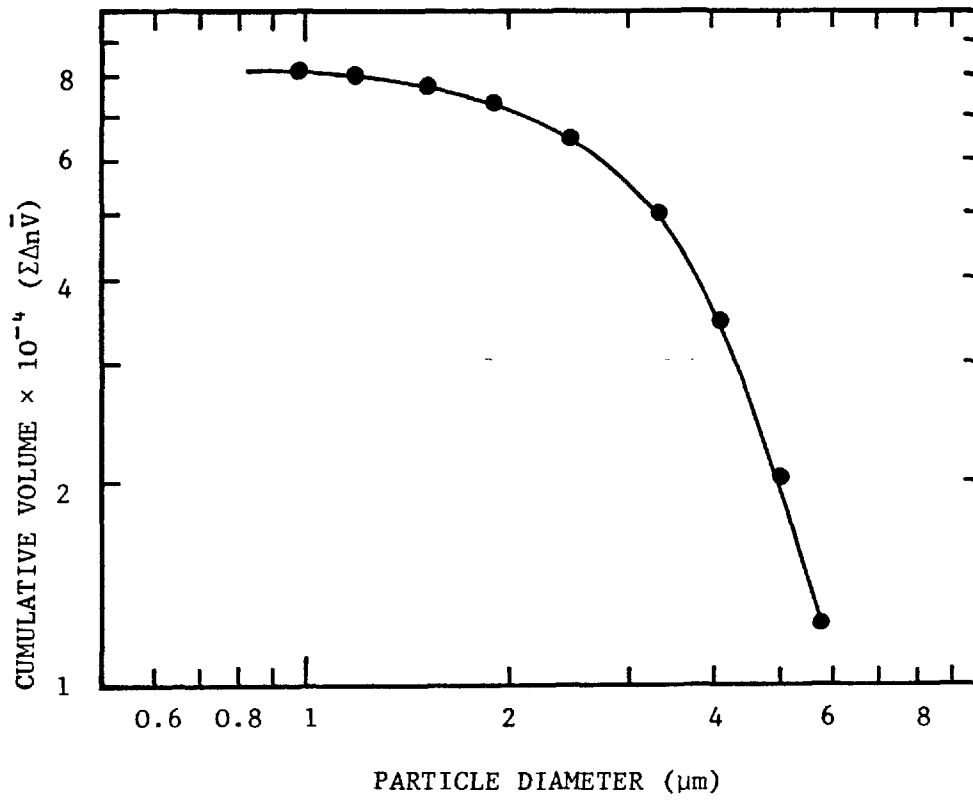


FIGURE 2.18: Cumulative volume of oil particles versus particle size as measured by Coulter Counter



A computer program was written (PROGRAM COULTER) to convert the results obtained from the Coulter Counter. The program calculates the geometric number mean and geometric volume mean diameter of a sample, as well as their standard deviations. Rate constants for different particle sizes and overall flotation rate constant calculations are also included in this program.

2.7 Microelectrophoresis Apparatus

A Rank Brothers Microelectrophoresis apparatus was used to measure particle electromobilities.

Calibration of different parts of the apparatus and adjustment of its illumination system were carried out according to the Instructions Manual.

Considering that the oil particles, although small, rise at moderate velocities as they move along the cell, the apparatus was set for use with flat cells.

Two quartz cells, 0.1×1 cm, were employed. Their dimensions were determined by means of the apparatus microscope itself and a travelling microscope.

To measure the effective inter-electrode distance, a solution of 0.1 M KCl was used. The resistance of the cells for this electrolyte solution was determined with a Wayne Kerr AC conductivity bridge (Autobalance Precision Bridge B331) operating at a frequency of 10^4 rad/s. The resultant electrical lengths were 8.323 and 6.876 cm, respectively.

To check the calibration of the apparatus, the electromobilities of human blood cells were measured in a phosphate buffer solution, pH = 7.4, at 25°C. Values obtained with either cell were -1.275 ± 0.095 and -1.280 ± 0.095 $\mu\text{m/s/V/cm}$ respectively. These electromobilities are lower than those reported in the literature; for

example, by Shaw (1969), -1.31 ± 0.03 , and by Collins (1975), -1.31 ± 0.09 . The discrepancy of results may be partly due to errors involved in the determination of the length of the cell, in particular, polarization effects arising during measurement of electrical resistance.

Cleaning of the cell was carried out as follows. First, it was thoroughly washed with tap water and then immersed for one hour in alcohol and chromic acid respectively. It was then left to soak for two hours in distilled water to leach out traces of chromate. Finally, it was soaked for one hour in NaOH N/10 and then rinsed and left in distilled water overnight.

An average of thirty measurements of transit times were made to calculate electromobilities of particles, fifteen on each stationary level.

2.8 Preliminary Experiments

To study the extent of flotability of the oil particles, several preliminary experiments were conducted using tap water as well as distilled water containing different salts.

2.8.1 Experimental Procedure

The procedure used throughout the experiments in this section is as follows.

The emulsion was prepared according to Section 3 of Appendix 1 and then poured into the column. The surfactant was usually added to the column at this stage, unless otherwise stated. The dispersion

was then diluted to 6 litres in the column by adding more water into the system. By switching on the recycle line the dispersion was stirred for $\frac{1}{2}$ hr before the start of the experiment. The stirring was needed to allow the surfactant to get adsorbed on the surface of the oil particles.

Venturi No. 1 was used to produce the bubbles. A liquid flow-rate of 2.8 l min^{-1} through the venturi was used. With the needle valve on the gas suction line fully open, the gas flowrate was $315 \text{ cm}^3 \text{ min}^{-1}$.

Complete mixing in the column was attained in less than $\frac{1}{2}$ minute after bubbling was started. This was checked through the addition of a small amount of dye to the column. Therefore, the concentration of oil particles could be assumed to be uniform throughout the column.

Samples were taken from the column at each 5 or 10 minutes, during the run, for concentration analysis. Each run lasted about 30 minutes.

The concentration of the oil particles in the samples was then measured by turbidimetry at 350 m μ . A Hitachi Perkin-Elmer spectrophotometer was used for this purpose.

2.8.2 Analysis of the Flotation Results

In order to represent the rate of flotation, a plot of $\ln C_0/C$ against time is prepared where

C_0 is the oil particle concentration at time zero, and

C is the oil particle concentration at time t .

Figures 2.19 and 2.20 show plots of $\ln C_0/C$ against time for different experiments with tap water and distilled water respectively. CTAB has been the surfactant used in these experiments.

As these figures show, all the experimental data points fall close to a straight line, suggesting a first order kinetics for the flotation of oil particles. Therefore, the slope of the best fitting

FIGURE 2.19: Plots of $\ln (C_0/C)$ versus time for experiments carried out in tap water

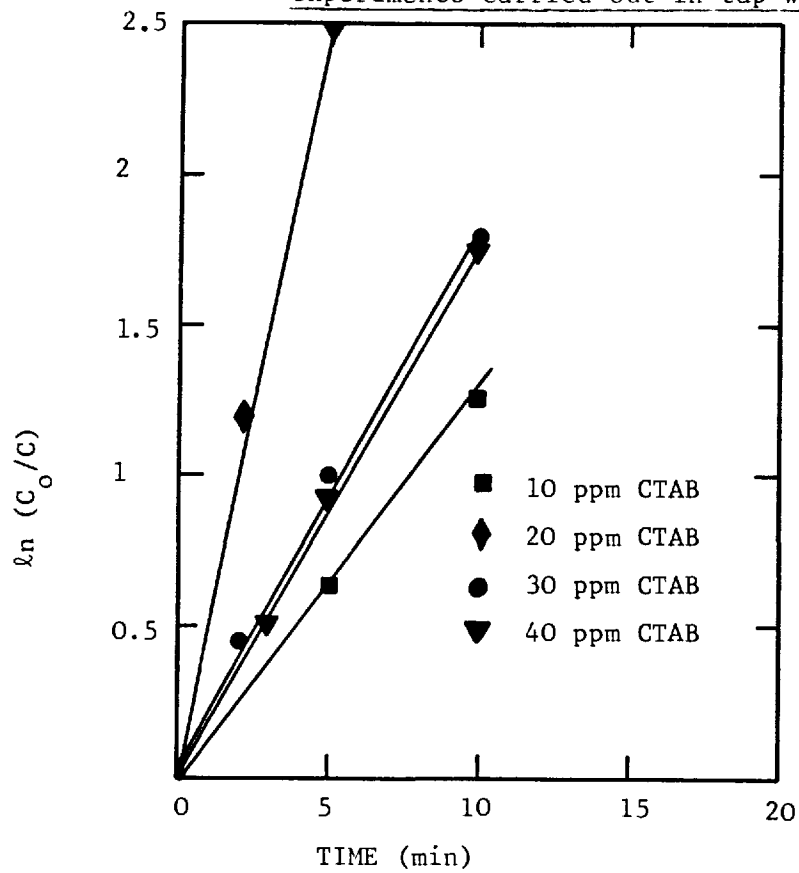
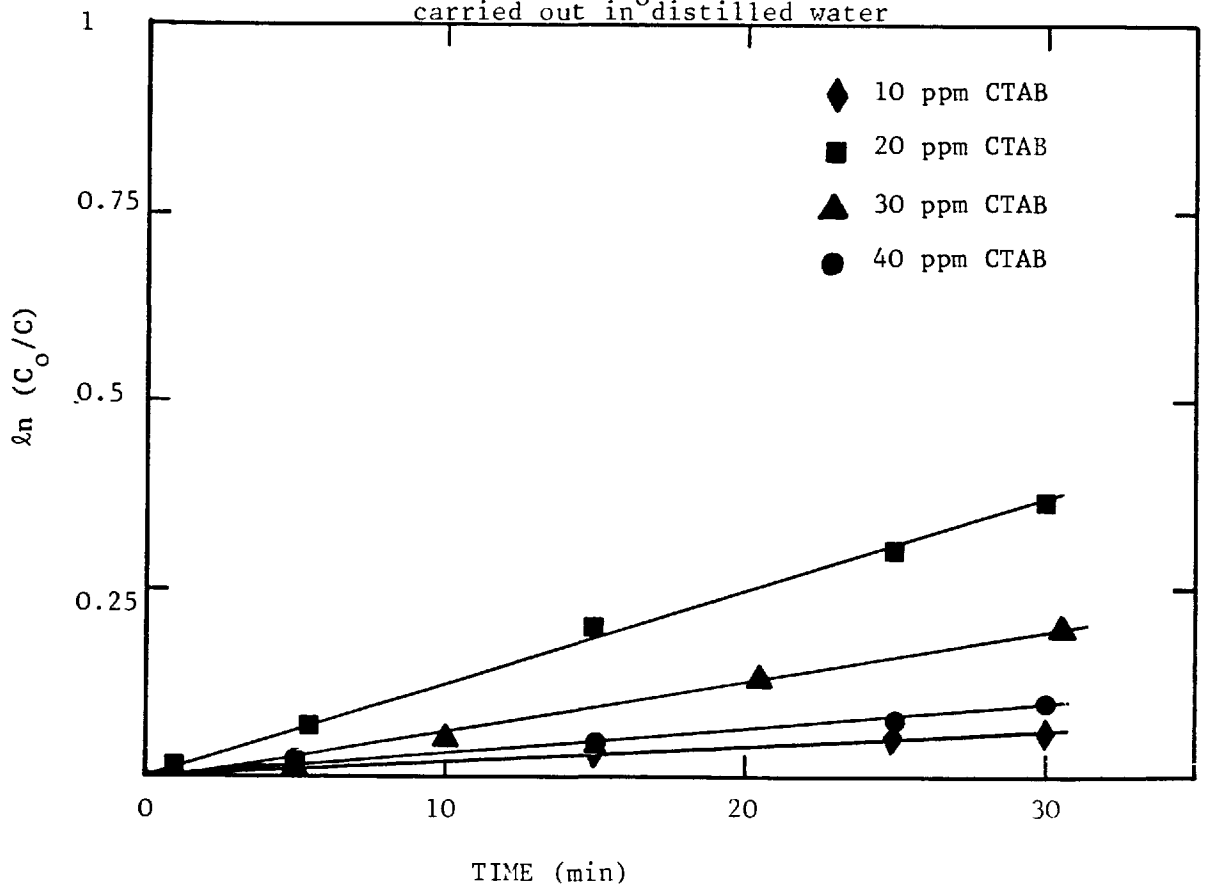


FIGURE 2.20: Plots of $\ln (C_0/C)$ versus time for experiments carried out in distilled water



straight line passing through the data points can be taken as the rate constant.

The results of flotation rate constants, k , for these experiments are shown in Table 2.3.

TABLE 2.3: Rate constants for distilled and tap water at different surfactant concentrations

Surfactant concentration ppm	rate constant in distilled water min^{-1}	rate constant in tap water min^{-1}
10	0.00194	0.124
20	0.00996	0.511
30	0.00744	0.178
40	0.00351	0.177

The results clearly show that the rate constants for tap water are much higher than those for distilled water. They also show the presence of a maximum rate constant in both cases for a certain concentration of the surfactant.

The higher rate of flotation in tap water warranted some further investigation on the cause of the discrepancy with distilled water. Tap water contains different salts and other impurities which can easily affect the rate of flotation. An analysis of London tap water provided by Thames Water Authority revealed the presence of different impurities in water (Table 2.4). A difference in pH between tap water ($\text{pH} = 8.2$) and distilled water ($\text{pH} = 5 - 6$) is another important factor to affect the rate of flotation.

TABLE 2.4: Analysis of London tap water. The values are in ppm.

Ammoniacal Nitrogen as N	Albuminoid Nitrogen as N	Nitrate Nitrogen as N	Oxygen abs from KMnO_4 4 hours at 27°C	B.O.D. 5 days at 20°C	Total Hardness CaCO_3	Alkalinity as CaCO_3	Calcium as Ca	Magnesium as Mg
0.090	0.105	7.8	1.44		264	154		6.7

Sodium as Na	Potassium as K	Chloride as Cl	Phosphate as PO_4	Silicate as SiO_2	Sulphate as SO_4	Natural Fluoride as F	Surface active material as Man-oxol OT	Turbidity (Silica scale)	Colour (Burgess units)
34	7.7	47	2.6	15	80	0.16		0.0	11

Surface tension for both tap water and distilled water at 25°C was measured. The values obtained were 67 and 72 dynes/cm respectively. This lower value of surface tension for tap water is obviously due to the presence of organic impurities in tap water.

The effect of salts and pH seemed, therefore, to be an obvious choice for further study. Several salts were separately considered to study their effects on the rate of flotation. These were NaCl , Na_2SO_4 , Na_2CO_3 and CaCl_2 .

2.8.3. Effects of Salts

In these experiments, the required amount of salts was first added to the distilled water. The emulsion was then prepared using this water following an adjustment of pH. The rest of the experimental procedure was the same as in Section 2.8.1.

Table 2.5 shows the effect of sodium chloride concentration on the flotation rate constant in distilled water. 20 ppm CTAB was used as surfactant.

Comparison of the results with Table 2.3 shows that the rates are slightly higher than those in pure distilled water but still much lower than in tap water.

TABLE 2.5: Flotation rate constants for different concentrations of NaCl. Surfactant concentration 20 ppm, pH = 6.

NaCl Mol gr/l	k min ⁻¹
0.005	0.0084
0.01	0.010
0.043	0.028
0.17	0.023
0.68	0.018

Upon using sodium sulphate as the salt, no drastic change was observed in the rates of flotation for the same system.

2.8.4 Effect of pH

The effect of pH was studied on a system with a concentration of 0.011 mol gr/l of Na₂SO₄ in distilled water using 20 ppm CTAB as surfactant. The results are shown in Table 2.6. There was a sharp increase in the rate constant as the pH was changed from acidic to basic.

TABLE 2.6: Effect of pH on flotation rate constants.
CTAB 20 ppm, Na₂SO₄ 0.011 mol gr/l.

pH	k, min ⁻¹
6	0.0115
7.5	0.0143
10	0.0610

Flotation rate constants as a function of salt concentration, Na_2SO_4 , for different pH are given in Figure 2.21.

Figure 2.22 also shows results obtained for Na_2CO_3 at pH = 10.5 - 11.5. The rate constants are comparable with those for Na_2SO_4 and a shallow maximum occurs at almost the same concentration for both salts.

Using a salt with a divalent cation, CaCl_2 lowered the rate of flotation for the same pH. The data related to this salt are also included in Figure 2.21.

Bearing in mind the difference in rate constants observed for tap water and distilled water, it is concluded that this difference cannot be accounted for solely on the basis of the parameters studied above.

2.8.5 Discussion on Preliminary Results

Theoretical and experimental investigation of flotation has shown that the rate constant is inversely proportional to the bubble size (Jameson et al, 1977). Therefore, a useful approach to analyse the effect of the above variables on the rate constant was to study their effect on bubble size.

In order to elucidate where the changes happen, the effect of salt and surfactant concentration as well as pH on bubble size was investigated.

Figures 2.23, 2.24 and 2.25 show the change of arithmetic number mean bubble diameter with respect to surfactant, salt concentration and pH for tap and distilled water.

A close comparison of the figures reveal clearly that the difference in the bubble size could not have been responsible for a high rate of flotation in tap water. As a matter of fact, the mean bubble size for distilled water containing salt and surfactant is

FIGURE 2.21: Flotation rate constant versus salt concentration, CTAB 20 ppm

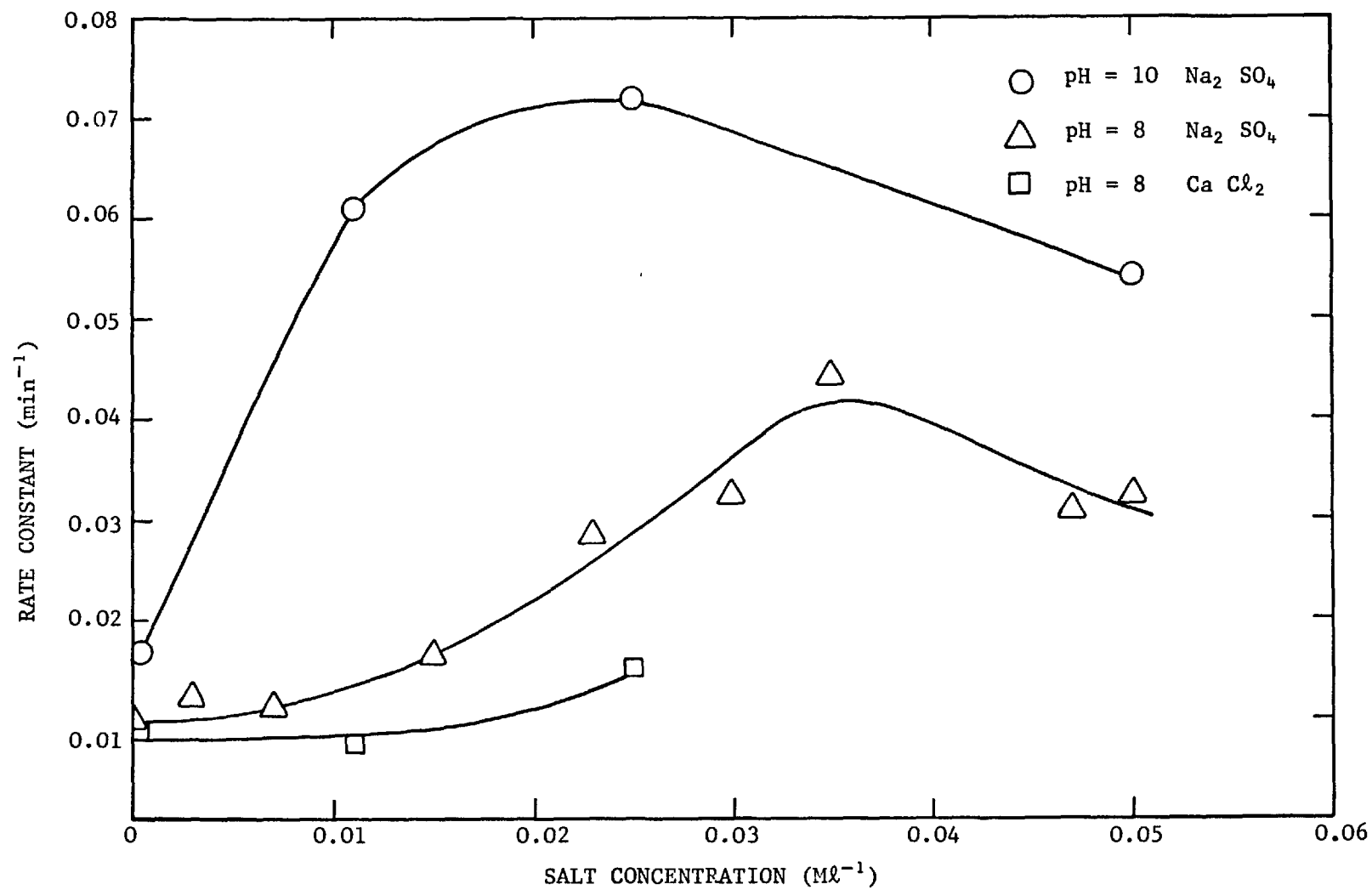


FIGURE 2.22: Flotation rate constant versus salt concentration.
Salt Na_2CO_3 , surfactant 20 ppm CTAB

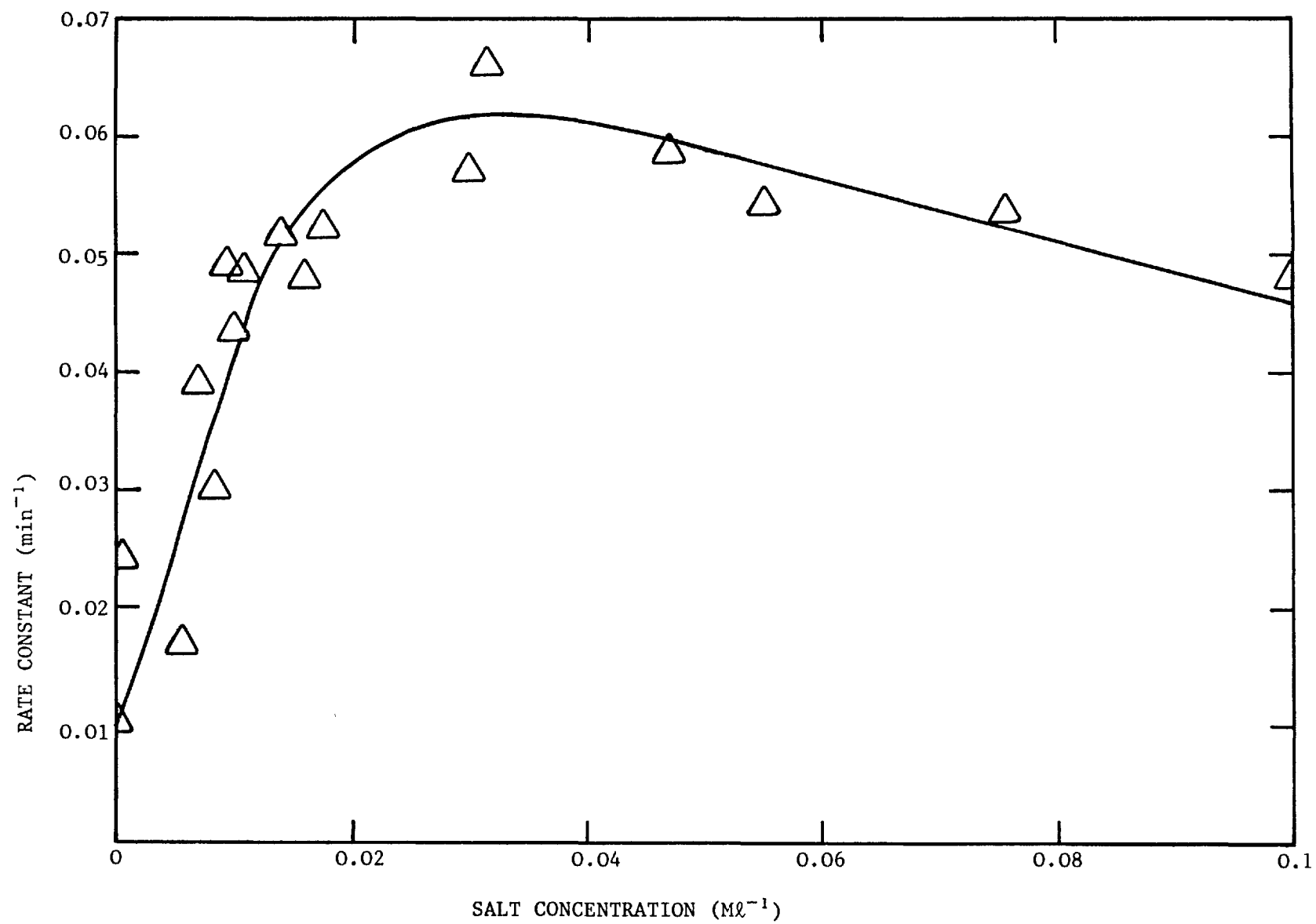


FIGURE 2.23: Bubble size versus surfactant concentration

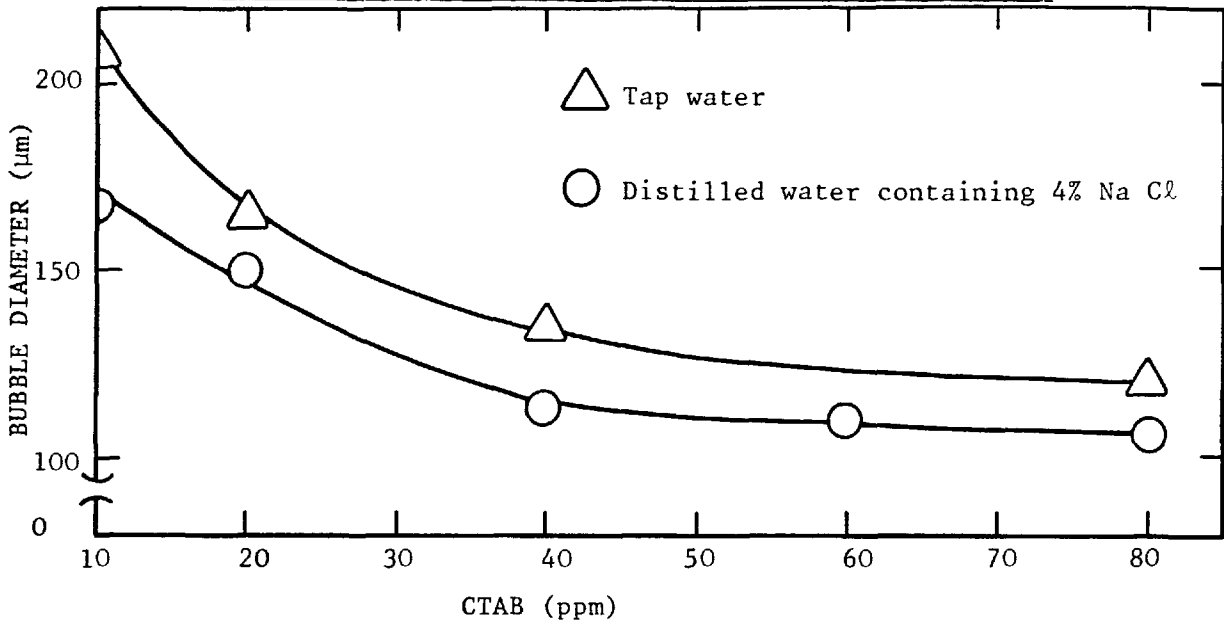
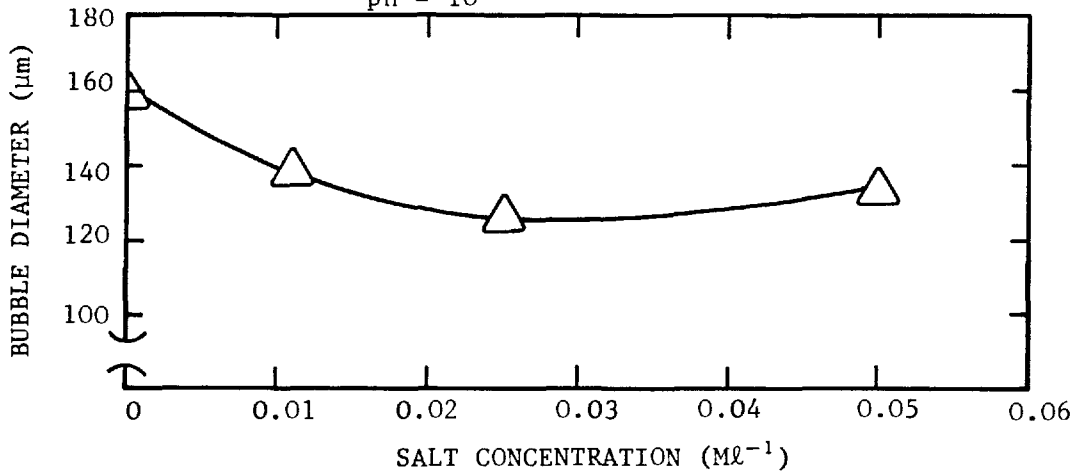
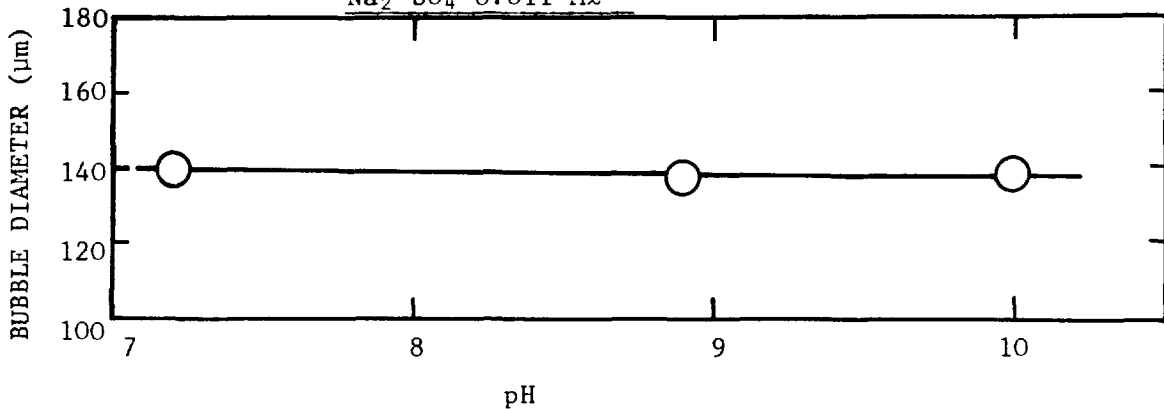


FIGURE 2.24: Bubble size versus sodium sulphate concentration, surfactant 20 ppm CTAB, pH = 10

FIGURE 2.25: Bubble size versus pH, surfactant 20 ppm CTAB, Na₂SO₄ 0.011 Ml⁻¹

slightly smaller than that for tap water. Therefore a higher rate of flotation could have been expected for distilled water.

The increase in rate constants in Figures 2.21, 2.22 and Table 2.5 could be attributed to an increase in adsorption of surfactant on the particle and bubble surfaces, for an increase in the concentration of salts. This effect has been studied by Connor and Ottewill (1971). They also showed that an increase in the concentration of salt (K Br) from 10^{-3} M to 5×10^{-2} M shifted the CMC of CTAB from 172 ppm to 32 ppm. The decrease in the rate constants in Figures 2.21 and 2.22 could also be attributed to a lowering of CMC of the surfactant and therefore, due to aggregation of the surfactant in the bulk of solution, in the form of micelles.

Figure 2.24 shows a slight increase in bubble size at a certain concentration of salt. This could also be explained on the basis of a depletion of surfactant as mentioned above.

In another attempt to find the reason for higher rates of flotation of oil particles in tap water, the electromobility of the oil particles was measured in both distilled and tap water. Table 2.7 shows the electromobilities, u_E , measured for tap and distilled water with and without the presence of surfactant.

TABLE 2.7: Electromobility of oil particles in tap and distilled water.

	u_E $\mu\text{m/sec/V/cm}$ no surfactant	u_E $\mu\text{m/sec/V/cm}$ 20 ppm CTAB
distilled water	-2.31	+4.81
tap water	-1.16	-0.48

The electromobilities measured in tap water are remarkably lower than those for distilled water. Therefore, it could be concluded that the presence of lower charges on oil particles in tap water would have resulted in lower repulsion amongst oil particles themselves as well as between oil particles and bubbles. The former results in a growth of particles upon coalescence which in turn affects the rate constant. This was actually observed in the experiments for tap water.

The rather poor collection for distilled water could be therefore attributed to the presence of higher charges on the oil particles.

Figure 2.26 confirms the presence of highly positively charged particles in distilled water, even at very low concentration of surfactant.

To find whether the salts present in tap water were responsible for the extent of the adsorption of the surfactant on the oil particles, the following experiment was performed.

The total salt content in Table 2.4 was translated into an equivalent concentration of CaCl_2 . The electromobility of the particles in distilled water was followed as a function of the concentration of Ca^{++} . At a concentration of ≈ 125 ppm, which was almost equivalent to the concentration of all the cations present in tap water, the electromobility of the particles was rather close to the corresponding value in tap water, Figure 2.27. Next, 20 ppm of CTAB was added to this dispersion; this resulted in the particles acquiring a very high positive charge, even larger than that obtained in the absence of salts (Table 2.7). These results are shown in Table 2.8.

Although the addition of salts has an interactive effect on the extent of surfactant adsorption on the oil particles, no explanation

FIGURE 2.26: Electromobility of oil particles in solutions of CTAB in distilled water

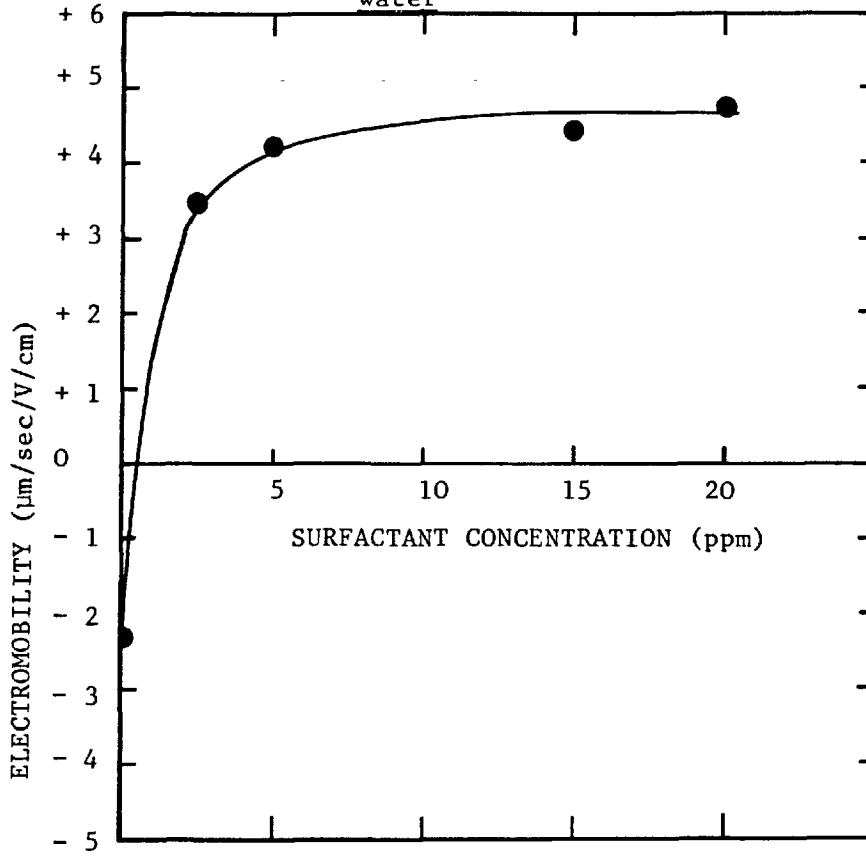
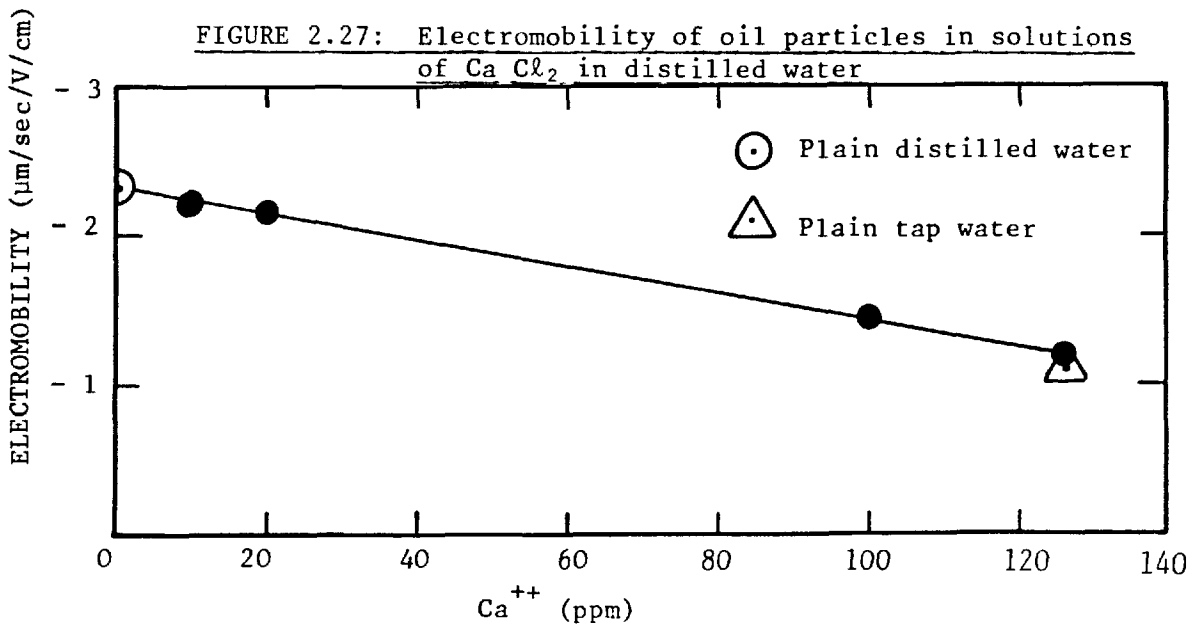


FIGURE 2.27: Electromobility of oil particles in solutions of Ca Cl_2 in distilled water



can be put forward for the behaviour of tap water.

TABLE 2.8: Electromobility of oil particles in tap water and
distilled water + salt

	u_E , $\mu\text{m/sec/V/cm}$ tap water pH = 8.1	u_E , distilled water + 125 ppm Ca^{++} pH = 5.5	u_E , distilled water + 125 ppm Ca^{++} pH = 8.05
no surfactant	-1.162	-1.196	-0.666
20 ppm CTAB	-0.48	+7.683	+7.782

The only possibility left to explain the oddity in behaviour of tap water would seem to be the adsorption of traces of surface active materials or particulate matter which are invariably present in tap water.

2.8.6 Choice of Surfactant

To enhance the flotability of oil particles in distilled water-salt systems, it was decided to study the possibility of charging the particles differently from the bubbles and therefore increasing the efficiency.

Using a combination of two surfactants in the system at the same time appeared to be one way to achieve this goal. In this case, an ideal situation would be that of employing a pair of cationic and anionic surfactants which are truly compatible.

On this basis, several contacts were made with different industries. They suggested various compounds which were thought to be useful in this system.

A reasonable choice of surfactant could probably be based on the value of its HLB.

HLB System

The HLB of a surfactant is an expression of its Hydrophile-Lipophile Balance, i.e. the balance of the size and strength of the hydrophilic (water-loving or polar) and the lipophilic (oil-loving or non-polar) groups of the compound. In general, surfactants consist of a molecule that combines both hydrophilic and lipophilic groups.

A surfactant that is lipophilic in character is assigned a low HLB number (below 9), and one that is hydrophilic is assigned a high HLB number (above 11). Those in the range of 9 - 11 are intermediate.

Intuitively, a surfactant with a low HLB would appear to be the proper choice for adsorption on the particles. Another, with high HLB could be employed for the production of bubbles.

In general, ionic surfactants are assigned higher HLB values and normally are soluble in water.

HLB values for most non-ionic surfactants can be calculated from either theoretical composition or analytical data (Griffin, 1955).

For the ionic surfactants, reliable HLB values can be obtained only by experimental methods. The experimental procedure can often be difficult and time consuming.

In the next section, the HLB values of the surfactants are mentioned if known. In those cases where a non-ionic surfactant was used for adsorption on the particles, a water soluble surfactant at the lowest available HLB was employed.

This was to prevent any insoluble material from disturbing particle size measurements.

Experimental Procedure.

The procedure obeyed for all the experiments in this section was as follows.

A solution of Na_2SO_4 in 6 litres of distilled water was prepared. The concentration of salt was adjusted to 300 ppm, i.e. almost equal to the total concentration of salts present in tap water.

The pH was then set at 8.1. The preparation of emulsion and adjustments for the gas and liquid flowrates were as in Section 2.8.1.

The surfactants used were of industrial quality due to unavailability of the pure equivalent materials.

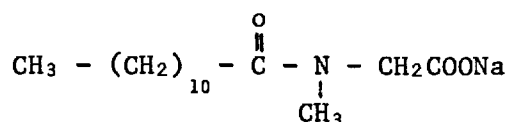
To examine the effect of different surfactants on bubble size, photographs were taken during the runs. These photographs were analysed (refer to Section 2.5 for instrument used) for qualitative observations only.

The efficiency of the surfactants was assessed by observing the change in turbidity in the column before and after an experiment. Also, photographs of samples taken from the column at zero and final times allowed examination of the decrease in population of the particles.

Different systems of surfactants as well as comments on their efficiency of flotation are given below.

2.8.6a Cationic-Anionic

The first choice was to try a cationic-anionic system. CTAB was used as the cationic surfactant. The anionic surfactant was from the family of Sodium Lauroyl Sacrosinates, commercially known as Hamposyl L (W. R. Grace Ltd). This compound is represented by the formula



This surfactant was suggested as an excellent foaming agent as well as compatible with quaternary ammonium compounds.

5 ppm of cationic surfactant was added to the flotation column. After sufficient time was allowed for adsorption the flotation experiment was started.

The anionic surfactant was added to produce the bubbles and possibly charge them differently from the particles. Therefore, 20 ppm of this surfactant was continuously added to the recycle stream entering the bubble generation device over a period of 20 minutes. A micropump (Metering Pumps Ltd) provided the flow of anionic solution to the column with a rate of 2.5 ml/min.

The rate of flotation was not too low, as compared with that obtained in some of the initial experiments. However, depletion of surfactant probably due to reaction between the two species was manifested through a growth in bubble size.

In a second attempt, another cationic surfactant from a family commercially known as Ethoquads was tried. The surfactant used was Ethoquad C/12. This is also a quaternary ammonium salt but possesses condensed ethylene oxide groups (2 molecules in this case) which render the molecule as a whole less cationic than ordinary quaternaries.

Ethoquads were also suggested to be somewhat more compatible with anionics than other cationics.

The rest of the procedure was kept the same as in the first experiment with CTAB.

The rate of flotation was found to be lower than with CTAB and the growth in bubble size was again observed.

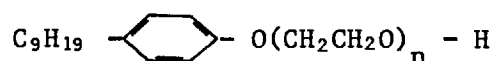
On the whole, the results were not satisfactory. The bubble size was observed to be too large. This was specially noticeable during the first five minutes of the experiment.

The bubble size was examined without the present of cationic surfactant and found to be reasonably smaller than in the other two experiments.

The amount of foamate obtained after 20 minutes was 50 ml for the CTAB system while for Ethoquad it was 90 ml.

2.8.6b Non-ionic-Anioic

In this case, a non-ionic surfactant was added to the emulsion. The surfactant was from a family of Nonylphenol Etoxylates (Henkel Chemicals Ltd), with the following chemical structure:



The properties of this family of surfactants can change according to n number. As n increases, they become more water soluble than oil soluble.

A compound of this group, industrially known as NP9, (n=9, HLB = 12.8), was employed as the non-ionic surfactant. It was suggested as a general emulsifier and stabiliser.

5 ppm of this surfactant was added to the emulsion before starting the flotation. The rest of the arrangements were exactly as before.

The efficiency was observed to be lower than before and the growth in bubble size was again noticed. The amount of foamate was almost 120 ml.

2.8.6c Non-ionic-Cationic

In another attempt, the non-ionic surfactant NP9 was added to the emulsion and a solution of CTAB was fed into the system to generate the bubbles.

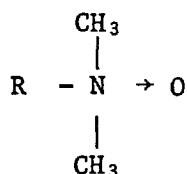
The bubbles were large and the rate of flotation was certainly lower than that obtained for the first two experiments with cationic-

anionic systems. The foam was bulky and the amount of foamate obtained was about 500 ml.

2.8.6d Cationic-Non-ionic

A last attempt to employ a pair of surfactants for flotation of oil particles was made with a pair of cationic and non-ionic compounds.

A non-ionic surfactant with high foaming characteristics was chosen to be fed into the bubble generation device. The surfactant was a tertiary amine oxide belonging to a group commercially known as Aromax (Akzo Chemie Ltd) with the following formula:



where R is a coco chain. The HLB of this compound is 18.7.

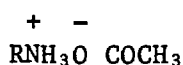
These compounds were considered to show considerable surface activity at very low concentrations and their foaming characteristics were comparable with those of anionics.

CTAB was used as the cationic surfactant to be adsorbed on the oil particles.

The experiment was performed as before. The rate of flotation was higher than for all of the previous experiments. The bubbles were larger at the beginning but decreased in size later. The amount of foamate was as high at 260 ml.

The same experiment was performed with another cationic surfactant, also used as a collector in flotation.

This surfactant was an acetate with the following formula:



A compound of this group, industrially known as Kemamine A-974 (Humko Products Ltd) with R being a technical tallow chain, was used.

The flotation experiment was carried out as before. The results were almost the same as with CTAB.

The high amount of foamate produced in these two cases was probably a disadvantage for these two systems.

The main drawback in all these experiments was the production of large bubbles during the first five minutes of the flotation run.

This could be attributed to two factors.

a) The surfactant available for bubble production at the start of any experiment was insufficient.

b) A reaction between the two surfactants present in the medium could have occurred, following by subsequent desorption of the surfactant already adsorbed on the particles.

The first alternative was checked by adding $\frac{1}{3}$ of the amount of surfactant normally added for bubbles, at the start of a run and the rest over a period of time. The bubbles looked considerably smaller.

Also as a check on point (b), only the foaming agent was added to the column following the procedure mentioned above. It was found that the bubbles were even smaller.

Some of the experiments were repeated by adding $\frac{1}{3}$ of surfactant to the column at zero time and the rest over 20 minutes. The rate of flotation was observed to be improved in almost all of them.

Discussion

Although the experiments in this section were performed on a rather qualitative basis, nevertheless their importance in revealing a few interesting points could not be underestimated. These could be classified as follows:

a) The presence of two different surfactants at the same time in the system results in a growth of bubble size, as compared with

the case when a single surfactant was used. This was probably due to reaction between the two species in solution.

b) Addition of part of the surfactant, e.g. $\frac{1}{3}$ of the total, to the flotation column prior to the experiment and the rest continuously, could greatly decrease the bubble size.

c) Out of the several combinations of surfactants used to enhance flotation of oil particles, the cationic-non-ionic system appeared to be the most effective.

d) The amount of foamate obtained from different experiments using different surfactants as frothers decreased in the following order:

anionic < non-ionic < cationic.

2.8.6e Single Surfactant System

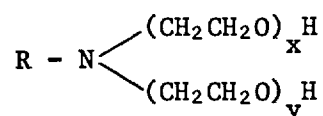
Interaction between surfactants in most of the Double Surfactant Systems appeared to be almost unavoidable. Therefore use of a suitable single surfactant could provide a more reasonable solution to the problem.

The idea of employing a cationic surfactant for flotation of negatively charged particles has been long used in the field of flotation.

In search of a proper single surfactant, series of ethoxylated amines were found whose properties varied from cationic to non-ionic depending on the numbers of ethylene oxide groups.

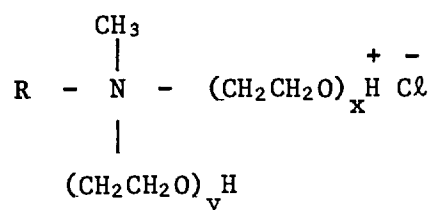
As the oil particles would be negatively charged, having a cationic surfactant would possibly be advantageous. On the other hand, a less cationic surfactant could assist in lower repulsion between the particles and bubbles.

Bearing these in mind, two groups of ethoxylated amines were considered. The first group was ethoxylated tertiary amines, industrially known as Ethomeen (Akzo Chemie Ltd), with the following chemical structure:



where $x + y$ changes from 2 to 15 and R is an alkyl group derived from fatty acids.

The second group were Ethoquads. These are ethoxylated quaternary ammonium salts with the following chemical structure:



where $x + y$ and R are defined as above.

These compounds are stable in both acidic and alkaline solutions and those with more non-ionic characteristics are not precipitated or inactivated by most inorganic ions.

One surfactant from each of these groups was tried separately for the flotation efficiency. These were Ethomeen C/25 and Ethoquad C/25. These compounds contain 15 ethylene oxide groups and C stands for coconut chain.

The flotation procedure was exactly as before, but only 20 ppm of surfactant was added to the emulsion.

The flotation rate was found to be reasonably good for both surfactant, although Ethoquad showed a better efficiency. The volume of foamate was as low as 100 ml for Ethoquad.

Consequently, Ethoquads were chosen for use in the subsequent experiments.

In order to have a well defined surfactant molecule, those compounds of this family with definite carbon alkyl chains, i.e. C₁₈ or C₁₂, were employed for the subsequent experiments.

2.9 Flotation Experiments

2.9.1 Experimental Procedure

To prepare for an experiment, 6 litres of distilled water were poured into a 10 l glass tank. The salt, sodium sulphate, was then added to the water and the pH was adjusted with a solution of N/1 NaOH. 1.5 litres of this water was then used to prepare the emulsion according to Section 2.4.2. Also a 10 cc sample was drawn from the tank to use as the blank for the measurements by Coulter Counter. The rest of the water was poured into the flotation column. The emulsion was next added following the addition of the surfactant. The mixture was left to stir for 15 minutes.

Electromobility measurements made at different time intervals showed that this time was adequate for particles to adsorb the equilibrium amount of the surfactant. These results are presented in Table 2.9.

TABLE 2.9: Electromobility of oil particles in 20 ppm Ethoquad 18/12 solution. Salt concentration $10^{-3} \text{ Ml}^{-1} \text{ Na}_2\text{SO}_4$.

Electromobility $\mu/\text{sec}/\text{V}/\text{cm}$	time minutes
$+3.235 \pm 0.095$	15
$+3.323 \pm 0.12$	40
$+3.367 \pm 0.095$	75
$+3.227 \pm 0.09$	110

After 15 minutes a sample was taken from the column as the zero time sample. The pH was measured at this stage and it was normally

found to be lower than the pH of the blank solution. Values reported for all experiments in the sections to follow correspond to this zero time measurement.

The flotation experiment was started by switching on the bubble generation line. The air flowrate was then adjusted by opening the needle valve and the liquid flowrate was set as required; this was considered the zero time for the experiment. Throughout these experiments, venturi 2 was used to produce the bubbles.

Samples were taken at 7, 15 and 25 minutes from the start of the experiment. These were analysed after a run for the particle size distribution and concentration in the Coulter Counter. The relevant settings for the Coulter Counter are given in Appendix 3.

Photographs were also taken of the bubbles through the flow cell at different times during a run, namely 2, 10 and 20 minutes. An average size for bubbles was then determined through analysis of these photographs.

A geometric volume mean was chosen as an appropriate mean size for the bubbles.

2.9.2 Surfactants Used

Two surfactants of the Ethoquad family were tried.

Experiments carried out under similar conditions for Ethoquad 18/25 and Ethoquad 18/12 are reported in Table 2.10. It can be observed that the rate constant is considerably higher for the former.

Average bubble sizes for both cases are also shown in the same table. The increased rate constant for Ethoquad 18/25 can be partly attributed to the markedly smaller bubble sizes produced for this system.

Therefore, this surfactant was used for all subsequent flotation experiments.

TABLE 2.10: Effect of surfactants on the rate of flotation.

Air flowrate 246 cc/min, pH 6.95, surfactant 20 ppm
and salt concentration $2 \times 10^{-3} \text{ M}\ell^{-1} \text{ Na}_2\text{SO}_4$, temp. 25°C

Surfactant	k, min^{-1}	bubble size, $\bar{d}_{gv}$ μm
Ethoquad 18/25	0.046	395
Ethoquad 18/12	0.0118	873

2.9.3 Gas Flowrate

To find the effect of gas flowrate on the rate of collection, some experiments were carried out with different gas flowrates. The results are shown in Table 2.11.

TABLE 2.11: Effect of gas flowrate on the rate of flotation

pH 6.95, salt concentration $2 \times 10^{-3} \text{ M}\ell^{-1} \text{ Na}_2\text{SO}_4$, temp. 25°C
Upstream liquid pressure $\approx 1.5 \text{ bar abs.}$

vacuum on the suction line mm Hg	liquid flowrate $\ell \text{ min}^{-1}$	glas flowrate $\text{cm}^3 \text{ min}^{-1}$	k min^{-1}	bubble size, $\bar{d}_{gv}$ μm
130	3.41	138	0.0324	—
110	3.28	150	0.0335	320
0	2.91	246	0.046	395

Two main factors were taken into account for the proper selection of gas flowrate; namely, bubble size distribution and amount of foamate.

Experiments carried out at large gas flowrate resulted in an increase in the rate constant. On the other hand, it was observed that both the bubble size and volume of foamate produced were larger

in this case. Considering that a compromise among these factors on the overall efficiency had to be reached, the gas flowrate was fixed at $150 \text{ cm}^3 \text{ min}^{-1}$.

2.9.4 Effect of pH

Some experiments were performed to find the effect of pH. The results are shown in Table 2.12. The change in the rate constants with pH does not appear to be significant. This could partly be attributed to the nature of the surfactant. Ethoquads are found to be stable in both acidic and alkaline solutions. However, a pH of 9.1 ± 0.1 was chosen in the subsequent experiments.

TABLE 2.12: Effect of pH on the rate of flotation.

$2 \times 10^{-3} \text{ M L}^{-1} \text{ Na}_2\text{SO}_4$ and 20 ppm Ethoquad 18/25, temp. 25°C

pH	k, min^{-1}
4	0.0327
6.95	0.0335
8.3	0.0383
9.1	0.040

2.9.5 Concentration of Surfactant

The effect of the concentration of surfactant on the rate constant was also investigated. The results are shown in Table 2.13.

TABLE 2.13: Effect of surfactant concentration on the rate of flotation. Concentration of salt $2 \times 10^{-3} \text{ Ml}^{-1}$ Na_2SO_4 and pH 9.1, temp. 24°C

Surfactant concentration ppm	k min^{-1}	foamate ml
10	0.0239	almost none
20	0.040	130
30	0.042	200
40	0.0290	270

The change in bubble size as a function of the concentration of surfactant is shown in Figure 2.28. Although the rate constant was higher in the case of 30 ppm concentration, on considering the larger amount of surfactant required and high volume of the foamate produced, a concentration of 20 ppm of surfactant was chosen for the subsequent experiments. As the results show, again a maximum in the rate constant is observed for a given surfactant concentration. The preliminary experiments with CTAB showed the same general behaviour although the maximum occurred at a different concentration of surfactant for this case.

To find the Critical Micelle Concentration of the surfactant, the conductivity of the surfactant solution was measured at different concentrations. The values of molar conductivities obtained are shown in Figure 2.29. An approximate value of $3 \times 10^{-4} \text{ mol/l}$ was obtained for the Critical Micelle Concentration.

2.9.6 Effect of Salt Concentration

Under the conditions obtained above, some experiments were carried out to study the effect of salt concentration from very

FIGURE 2.28: Bubble size vs. surfactant concentration

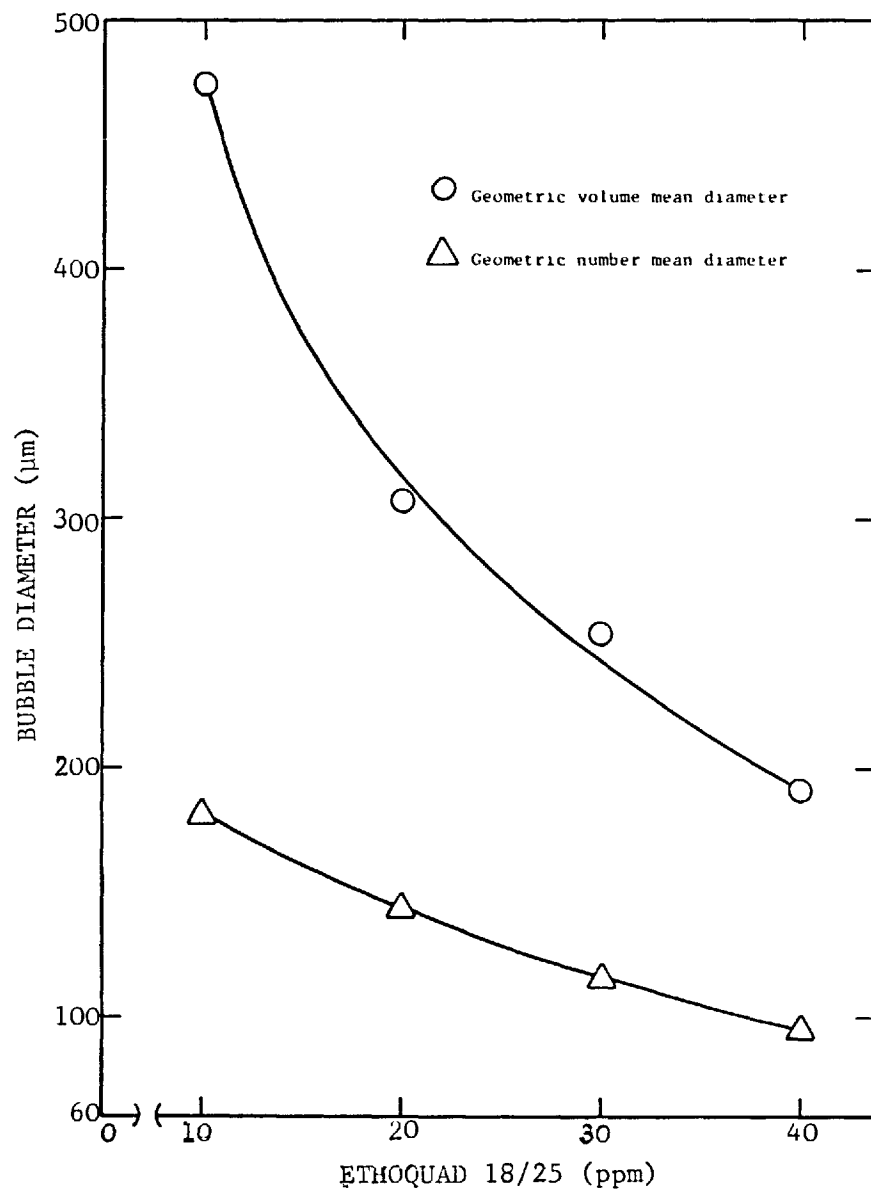
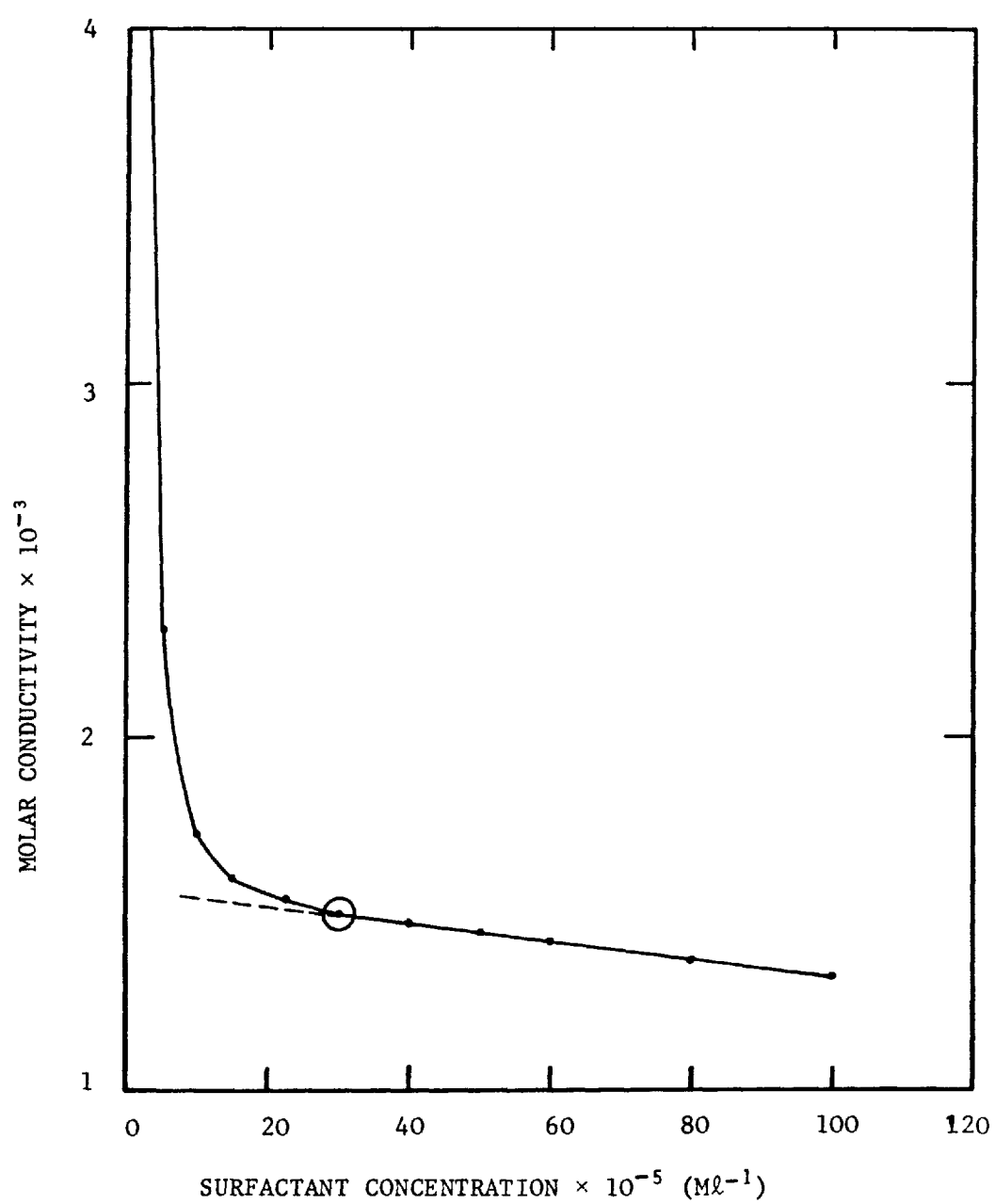


FIGURE 2.29: C.M.C. determination for Ethoquad 18/25



dilute solutions up to a concentration of 4% Na_2SO_4 .

The variation in rate constant as well as bubble size and electromobility of particles as a function of concentration of salt is shown in Figures 2.30, 2.31 and 2.32.

The rate of flotation is obviously seen to increase with salt concentration. The bubble size appears to be almost constant up to a certain concentration, about 10^{-2} Ml^{-1} , and sharply decreases afterwards. The electromobility of the particles obviously decreases as the amount of salt increases.

2.9.7 Effect of Bubble Size on the Rate of Flotation

One way of studying the effect of bubble size on the rate of flotation is to produce conditions such that every physical and chemical factor, including gas flowrate, is constant except bubble size.

In our system, such conditions could only be met by employing different bubble generation devices. By an appropriate change in the design of the venturi, a different bubble size could be produced while keeping the gas flowrate constant through controlling the vacuum on the suction line.

To study the effect of bubble size, some experiments were carried out in tap water and the results are shown in the tables below.

TABLE 2.14: Effect of Bubble Size on the Rate of Flotation

Air flowrate $146 \text{ cm}^3 \text{ min}^{-1}$, concentration of Ethoquad
20 ppm, temp. 24°C

Venturi number	Vacuum on the suction line mm Hg	liquid flowrate l min^{-1}	$\bar{d}_{gv}$ μm	k min^{-1}
2	110	3.28	328	0.0848
5	50	3.28	388	0.0588

FIGURE 2.30: Flotation rate constant versus sodium sulphate concentration, surfactant 20 ppm
Ethoquad 18/25, pH = 9.1, temp. 25°C

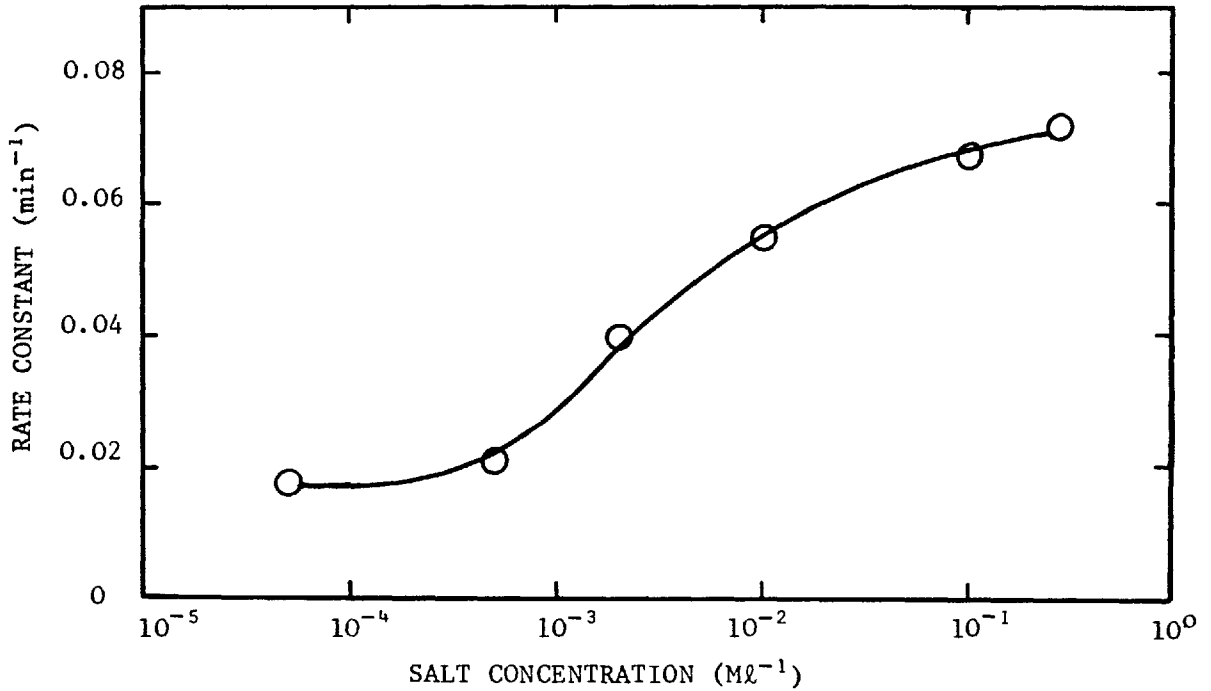


FIGURE 2.31: Bubble size versus sodium sulphate concentration, surfactant 20 ppm
Ethoquad 18/25

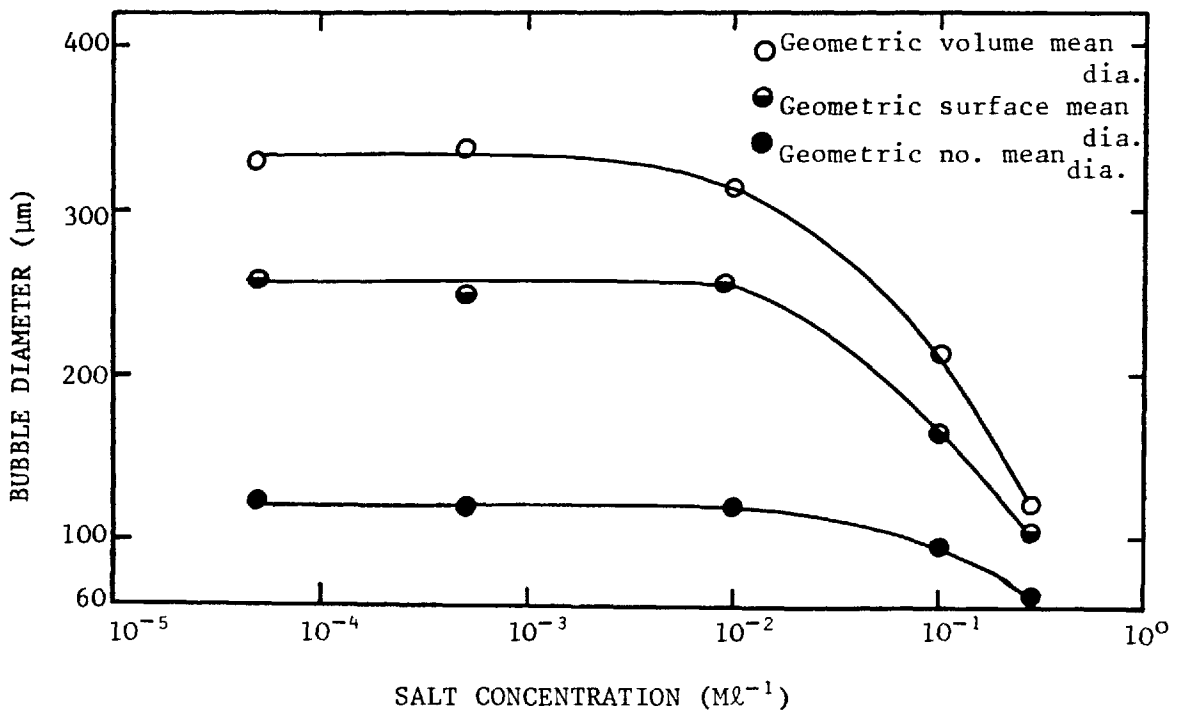


FIGURE 2.32: Electromobility of oil particles versus sodium sulphate concentration, surfactant 20 ppm Ethoquad 18/25, pH = 9.1

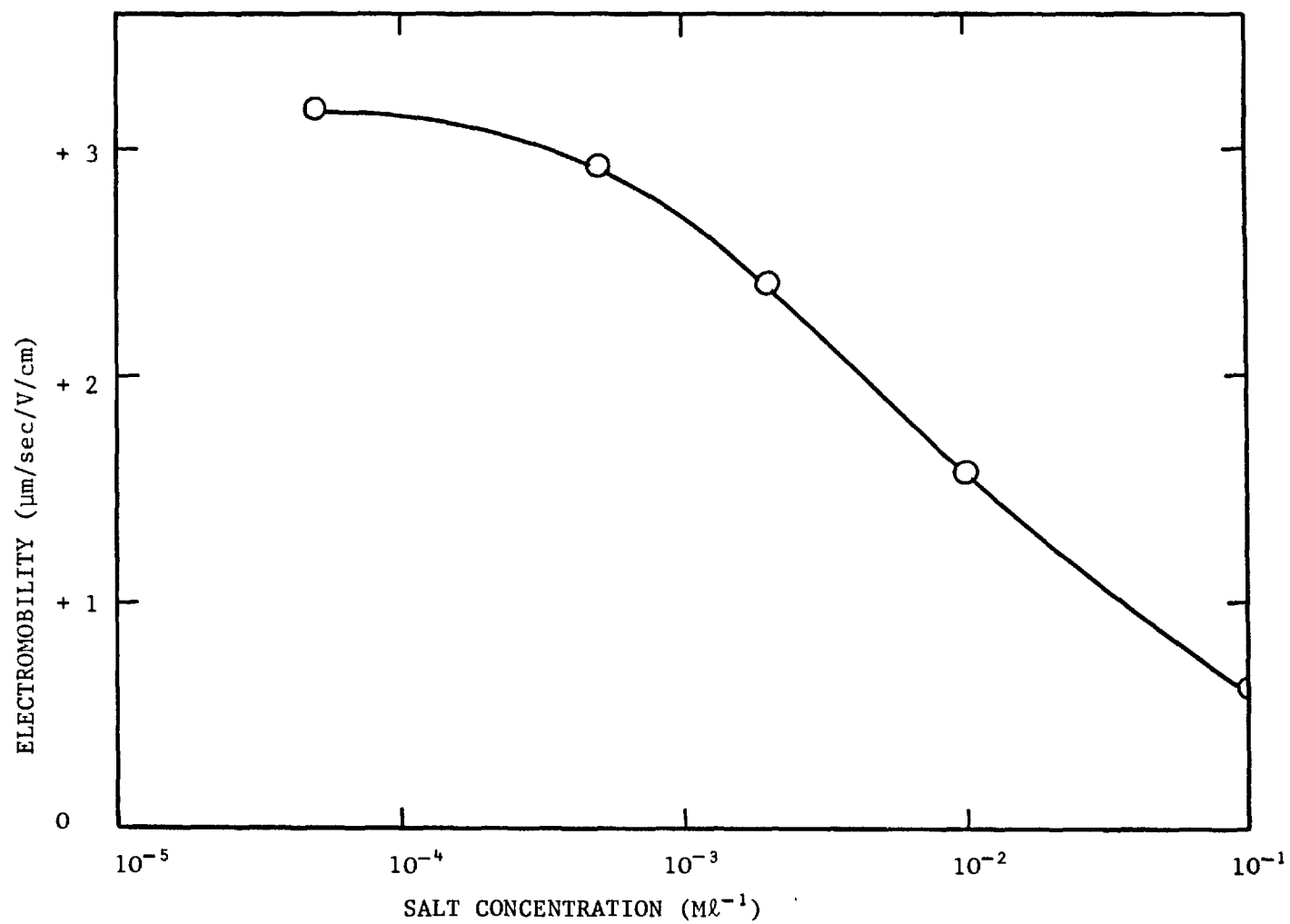


TABLE 2.15: Effect of Bubble Size on the Rate of FlotationAir flowrate $110 \text{ cm}^3 \text{ min}^{-1}$, concentration of Ethoquad20 ppm, temp. 24°C

Venturi number	Vacuum on the suction line mm Hg	liquid flowrate $\ell \text{ min}^{-1}$	$\bar{d}_{gv}$ μm	k min^{-1}
5	90	3.41	312	0.069
6*	10	3.41	322	0.064

*This was a single hole venturi whose diameters of throat and hole were 1.8 and 0.5 mm, respectively.

In both cases it can be observed that increasing the bubble size decreases the rate constant.

2.9.8 Study of Coalescence of the Particles in the Flotation Column

To investigate whether the particle size distribution was constant during a run, an experiment was arranged to simulate the condition in the flotation column, separately.

An emulsion of oil in water was prepared in the usual way. After taking the emulsion to six litres, part of this volume, 2 litres, was poured into a beaker. The surfactant was added and the system gently stirred by hand.

After 15 minutes of stirring, a sample was taken, zero time sample, and the solution was then stirred with a stirrer at a low speed, 250 rpm, to simulate the effect of stirring caused by the bubbles on the emulsion.

Samples were then taken at 7, 15, and 25 minutes and analysed by Coulter Counter to follow the rate of coalescence. The rate of coalescence was found to be very pronounced at $10^{-1} \text{ M Na}_2\text{SO}_4$. The results for this particular concentration of salt are shown in the

second column of Table 2.16.

The values reported $(N/No)_1$, correspond to the ratio between the total particle count of samples at time, t , to the total count at zero time.

The value of N/No has also been measured for an undisturbed dispersion inside a test tube. The test tubes were kept undisturbed for a length of time corresponding to that of the samples withdrawn from the actual run awaiting analysis by Coulter Counter. The results are presented in the last column of Table 2.16. Both stirring and shaking of the test tubes between sampling and actual measurement enhanced coalescence instead of keeping the particles in suspension.

TABLE 2.16: Coalescence of oil particles. Salt concentration
 $10^{-1} \text{ Ml}^{-1} \text{ Na}_2\text{SO}_4$, surfactant concentration 20 ppm
Ethoquad 18/25, pH 9.1.

time, t , minutes	$(N/No)_1$	$(N/No)_2$
0	1	0.96
7	0.86	0.94
15	0.78	0.93
25	0.67	0.96

The value of $(N/No)_1$ for a salt concentration of $10^{-2} \text{ M Na}_2\text{SO}_4$ or less was never below 0.96.

2.10 Discussion

An examination of Figures 2.30, 2.31 and 2.32 presented in Section 2.9.6 enables a few conclusions to be drawn regarding the effect of salt addition on the flotation rate. Thus, it can be concluded that an increase in salt concentration, for a given surfactant concentration in the system, has led to

- a) A decrease in particle electromobility (zeta potential)
- b) An increase in adsorption of surfactant at the air/water interface.

The effect of these factors on the flotation rate are in turn discussed below.

a) Figure 2.32 shows that the oil particles are always positively charged in the whole range of salt concentrations employed in this work, with particle electromobility decreasing with increasing salt concentration. The bubbles, on the other hand, can be assumed to carry a similar charge due to surfactant adsorption.

Figure 2.31 shows that for salt concentrations below 10^{-2}M the bubble size remained almost constant. Therefore, the increase in flotation rate constant for this region of salt concentration, as observed in Figure 2.30, could be solely attributed to a decrease in repulsion between bubble and particle.

b) It is known that an increase in inorganic electrolyte concentration can also enhance adsorption of surfactant at the air/solution interface, and therefore reduce the bubble size distribution produced in the flotation column. Figure 2.31 reflects such behaviour for concentrations above 10^{-2}M . The increase in the flotation rate constant observed in Figure 2.30 for this concentration range is therefore the result of the combined effects of a decrease in electromobility as well as bubble size.

The effect of surfactant concentration, for a given electrolyte

formulation, on the rate of flotation is reported in Section 2.9.5, Table 2.13. It can be noticed that a maximum in the rate constant is obtained for a particular surfactant concentration. The bubble size, as shown in Figure 2.28, decreases over the whole range of surfactant concentrations studied. Two possible reasons could be put forward to account for this maximum in the flotation rate. Thus, increased adsorption of surfactant on both the air/water and oil/water interface could have overcome the effect of bubble size reduction through simultaneous increase of repulsion between particle and bubble beyond a given surfactant concentration.

A second effect, rather more subtle, appears upon operating the flotation column. Above a particular surfactant concentration it is observed that the bubbles are so close together in the column that they no longer move like isolated entities but rather like a solid piston carrying solution into the froth layer. The particle recovery becomes dependent on this sweeping action as well as on the particle-bubble attachment. From the results obtained here, i.e. a reduction in rate constant, the collision and attachment appear to have become less effective.

3.1 Introduction

In this chapter, the theoretical background leading to the calculation of capture efficiency by a single bubble is described.

If it is assumed that all the particles which hit the bubbles are actually collected, that is, if the adhesion efficiency, E_a , is taken as one, the collection efficiency, E , can be approximated by E_c , the collision efficiency.

Theoretical investigation of the collection of fine particles by spherical collectors has received considerable attention in the past ten years. Although the major contribution in this field has come from valuable studies carried out on filtration, similar theoretical approaches have been undertaken by investigators in both filtration and flotation processes.

Due to the complexity associated with the problem of describing the flow field past an assemblage of spheres, the simpler problem of a single sphere has been closely studied.

Two different approaches have been used in calculations of collection efficiency. In one, to calculate E , the rate of deposition, I , is determined by integrating the particles flux resulting from the combined convective-diffusion transport of particles over the collector surface. The capture efficiency is defined as the ratio of the actual deposition rate to the rate of convection at large distances upstream from the collector,

$$E = \frac{I}{\pi r_c^2 U C_\infty}$$

where r_c is the radius of the collector and U and C_∞ are the velocity of fluid and the concentration of the particles far from the collector.

The other approach referred to in the literature as the collision approach, is based on calculating the grazing trajectory of a particle as it approaches a collector. It does not account for Brownian motion of particles.

A grazing trajectory is found, i.e. that for which the particle just grazes the collector as it crosses its equatorial plane. If this trajectory is a distance, y_∞ , away from the system's axis of symmetry at infinity, all the particles lying within y_∞ from the axis can collide with the collector. The collision efficiency can be written as,

$$E_c = \frac{y_\infty^2}{(r_c + r_p)^2}$$

where r_p is the radius of particles.

Spielman and Goren (1970, 1971) calculated the capture efficiency of non-Brownian particles by a spherical collector using the trajectory approach based on the creeping flow approximation. In their analysis, they also included the attraction forces by using an expression for non-retarded London/van der Waals forces between the particle and the collector.

Spielman and Fitzpatrick (1973) generalised this solution by incorporating the gravitational forces on the particle to the analysis.

Their results were presented as plots of capture efficiency versus two dimensionless groups reflecting the effects of attraction and gravitational forces. These are

$$N_{Ad} = \frac{Ar_c^2}{9\pi\mu_c U r_p^4} \quad ; \quad N_{Gr} = \frac{2(\rho_p - \rho_f)gr_c^2}{9\mu_c U}$$

where A is the Hamaker constant, ρ_p and ρ_f are particle and fluid densities, g is the acceleration due to gravity and A_c is a parameter characterising influence of neighbouring collectors and is equal to 1 for a single isolated sphere.

Prieve and Ruckenstein (1974) carried out a comprehensive work on calculation of collection efficiency of Brownian particles suspended in a viscous fluid by a spherical collector. They calculated the rate of deposition of the particles over the surface of the collector under the combined action of convective-diffusion, gravitational and London forces, based on the creeping flow approximation.

Spielman and Cukor (1973) investigated the effect of intermolecular forces on the capture efficiency of neutrally buoyant non-Brownian particles also within the limits of the creeping flow approximation using the trajectory approach. Their expression for intermolecular forces accounted for both the non-retarded London attraction and diffuse double layer interactions for equal potentials on particle and collector. They produced their results in the form of plots of capture efficiency versus a dimensionless number, N_ζ , representing the repulsion between particle and collector for different values of attraction (N_{Ad}) and for a given solution ionic strength. N_ζ is defined as

$$N_{\zeta} = \frac{3\epsilon\zeta_1\zeta_2r}{2A}P$$

Here, ζ_1 and ζ_2 are the ζ potentials of the surfaces and ϵ is the dielectric constant of medium.

Ruckenstein and Prieve (1973) calculated the rate of deposition of Brownian particles considering the effects of diffusion, convection and intermolecular forces for several geometries of collector (sphere, cylinder, rotating disc). The terms they considered for intermolecular interactions were similar to those of Spielman and Cukor.

A characteristic common to all the theories developed for capture efficiency as applied to filtration, is that the hydrodynamic corrections to the drag force are always introduced for the particular case of a small particle approaching a plane surface.

Using the trajectory approach, Fonda and Herne (1957) were the first to solve the equations of motion of a small particle approaching a larger collector assuming both Stokes and potential flow around the collector, and calculated the grazing trajectory and consequently the collision efficiency. In their analysis, the gravitational forces were neglected as their results were intended to apply to mist collection.

Flint and Howarth (1971) extended the approach of Fonda and Herne to the case of froth flotation. They introduced the additional term of acceleration due to gravity to the particle's equations of motion and found the grazing trajectory and the collision efficiency for both potential flow and Stokes flow around a bubble. They assumed a particle was captured if its centre grazed the surface of the bubble. Their expression for

the collision efficiency was

$$E_c = \frac{y_\infty^2}{r_b^2}$$

where r_b is the radius of the bubble.

Reay and Ratcliff (1973) attempted the problem of calculating the collision efficiency in a similar way. They assumed that a particle whose surface grazed the surface of a bubble should be collected.

In both solutions of Flint and Howarth and Reay and Ratcliff, the intermolecular forces and hydrodynamic corrections have been neglected.

In this chapter, the necessary steps for the calculation of trajectory and collision efficiency based on the definition of Reay and Ratcliff are described.

The equations of motion are solved for an arbitrarily moving particle and bubble in an unbounded otherwise undisturbed fluid assuming creeping flow around both particle and bubble, i.e. $Re < 0.5$. Both particle and bubble are assumed to be rigid spheres. This assumption is justified as surface active substances which are always present in flotation processes tend to immobilise the surface. It is observed that bubbles as large as 1 mm rise as "solid" spheres in solutions containing traces of surface active agents (Fuerstenau and Wayman, 1958).

The hydrodynamics interactions are introduced for two spheres of comparable size rather than for a sphere and a plane.

Terms describing fully retarded London/van der Waals attraction, double layer repulsion as well as gravitational forces, are incorporated into the equations of motion.

The arbitrary motion of a sphere in a two spheres system

is approximated by its motion along and perpendicular to the line of centres. The torque on the spheres is assumed to be zero.

In Section 3.2 of this chapter, the procedure leading to calculation of corrections to the drag force on one sphere due to the presence of the other is given.

The intermolecular forces are described in Section 3.3. An expression is derived to calculate the correction factor to the London/van der Waals attractive forces between two spheres to allow for retardation. The assumption of constant potential on the spheres as they approach each other has been considered for the calculation of intermolecular repulsion forces.

3.2 , Hydrodynamic Forces in Two Spheres System

In this section the motion of two spheres in a viscous fluid is discussed. The spheres are assumed to be moving slowly through an unbounded viscous fluid in an arbitrary manner. The fluid is also assumed to be incompressible and at rest at infinity.

The Navier-Stokes equations of motion for an incompressible Newtonian fluid are given in vectorial notation by,

$$\frac{\partial \underline{u}}{\partial t} + \underline{u} \cdot \underline{\nabla} \underline{u} + \frac{1}{\rho} \underline{\nabla} p = \nu \nabla^2 \underline{u} \quad (3.1)$$

$$\underline{\nabla} \cdot \underline{u} = 0 \quad (3.2)$$

where $\underline{u}$ and p are the local fluid velocity and pressure, and ν and ρ are the fluid kinematic viscosity and density.

In many applications, these equations can be linearised when the inertial term $\underline{u} \cdot \underline{\nabla} \underline{u}$ is small compared with the viscous term, $\nu \nabla^2 \underline{u}$. The time dependent term, $\frac{\partial \underline{u}}{\partial t}$, on the other hand can also in some cases be neglected.

Rushton and Davies (1978) have assessed the order of magnitude of inertial, acceleration and viscous terms for two particle problems. They showed that the inertial and local acceleration forces, for this system, may be neglected compared with viscous forces, provided $Re \ll 1$.

Assuming that $Re \ll 1$, equations 3.1 and 3.2 can be simplified as follows:

$$\frac{1}{\rho} \underline{\nabla} p = \nu \nabla^2 \underline{u} \quad (3.3)$$

$$\underline{\nabla} \cdot \underline{u} = 0 \quad (3.4)$$

Equation 3.3 can be written in terms of Stokes stream function as

$$\phi^4 \psi = 0 \quad (3.5)$$

where

$$\phi^2 = \frac{\partial^2}{\partial z^2} + \rho \frac{\partial}{\partial \rho} \left(\frac{1}{\rho} \frac{\partial}{\partial \rho} \right)$$

and (ρ, z) are cylindrical coordinates.

As the governing equations are linear, the solution for the fluid motion caused by the spheres moving in an arbitrary direction can be obtained by combining the solution for the motion of the spheres parallel to their line of centres and that for the motion perpendicular to it.

Both of these problems have been studied by several investigators. In the case of the motion of two spheres along their line of centres, (axisymmetric flow), the exact solution for the flow obtained by Stimson and Jeffery (1926) is probably one of the most comprehensive works in this field. They solved the problem for two arbitrary solid spheres translating at the same velocity along their line of centres and produced numerical results for equal spheres. Haber et al (1973) extended Stimson and Jeffery's solution to the case of two different spheres moving at different velocities.

Approximate solutions to this problem based on the method of reflections have been given by Happel and Brenner (1965) and Hestroni and Haber (1978). The convergence of these solutions is poor at close surface to surface distances. Approximate solution for the axisymmetric flow of a solid sphere touching a plane as well as an exact solution for two touching solid spheres of arbitrary sizes has been given by Goren (1970). An exact solution for two touching fluid spheres moving along their line of centres has been given by Reed and Morrison (1974).

An exact solution for the motion of spherical solid particles, liquid droplets or gas bubbles along their line of centres has

recently been given by Rushton and Davies (1978).

Their solution is based on the stream function obtained by Stimson and Jeffery. A complete review of the current state of knowledge of axisymmetric flow is also included in their paper.

The problem of the motion of two spheres perpendicular to their line of centres (asymmetrical flow) has received comparatively less attention. A summary of the approximate solutions based on the method of reflections available up to 1965 is given by Happel and Brenner (1965). As for the case of axisymmetric flow, the convergence is again poor for the method of reflections.

Goldman, Cox and Brenner (1966) were the first to present an exact solution for two equal spheres moving perpendicular to their line of centres. They based their solution on the work by Dean and O'Neill (1963) for the translation of a sphere parallel to a plane wall bounding a semi-infinite viscous fluid. Wakiya (1967) generalised the solution given by Dean and O'Neill for the case of two spheres of arbitrary sizes moving vertically to their line of centres. O'Neill and Majumdar (1970) solved the problem numerically on the basis of Wakiya's work and produced for the first time exact results for unequal spheres moving at different velocities.

Hestroni and Haber (1978) later presented an approximate solution based on the method of reflections for two spherical droplets. Their results agreed reasonably well with those of the exact solution up to a surface to surface distance of one particle radius.

All solutions pertinent to the motion of two spheres have been facilitated through the use of bipolar coordinates (ξ, η, ϕ) . Their relation to cylindrical coordinates (z, ρ, ϕ) is defined through,

$$\rho = \frac{c \sin \xi}{\cosh \xi - \cos \eta} ; z = \frac{c \sinh \xi}{\cosh \xi - \cos \eta} ; \phi = \phi$$

Two spheres external to each other with centres on the z axis and at distances d_1, d_2 from the origin and on opposite sides of the origin can be defined by $\xi = \alpha, \xi = \beta (\alpha > 0, \beta < 0)$; α, β and the constant c may be chosen so that these spheres have any radii, r , and any centre to centre distance, $d_1 + d_2$, greater than the sum of their radii, so that

$$\begin{aligned} r_1 &= c \operatorname{cosech} \alpha, & r_2 &= -c \operatorname{cosech} \beta \\ d_1 &= c \coth \alpha, & d_2 &= -c \coth \beta \end{aligned}$$

In Appendix 4 the bipolar coordinate system is described in more detail.

The expression for the force required to maintain the motion of the spheres 1 and 2 at a given velocity is

$$F_i = 6\pi\lambda_i \mu v_i R_i \quad i = 1, 2 \quad (3.6)$$

Here, λ_i is defined as the ratio of the force required to maintain the motion of sphere i in the presence of the other sphere to the force which would be required to maintain its motion with the same velocity if the other sphere were at an infinite distance. μ is the fluid viscosity and R_i and v_i are the radius and velocity of the sphere respectively.

The correction factor to the force exerted by the fluid on the spheres, λ_i , for both motions along and perpendicular to the lines of centres can be obtained following the solution of the equations of motion.

In Section 3.2.1 of this chapter, the problem of the motion of two unequal solid spheres moving with different velocities along their

line of centres is given. The exact solution for two solid spheres is obtained on the basis of Stimson and Jeffery's solution (1926).

In Section 3.2.2, the motion of two unequal solid spheres perpendicular to their line of centres is considered. The exact solution to this problem is obtained on the basis of Wakiya's (1967) approach.

3.2.1 Motion of Two Spheres along their Line of Centres

The procedure of Stimson and Jeffery (1926) is chosen here to calculate the forces necessary to maintain the motion of two spheres along their lines of centres. The system considered consists of two rigid spheres, 1 and 2. Their radii are R_1 and R_2 and they are moving along their line of centres with velocities v_1 and v_2 respectively (Figure 3.1). The flow field is assumed to be Stokesian and the fluids involved are homogeneous, incompressible, Newtonian and have constant physical properties.

Neglecting inertia terms, the differential equation to be satisfied by Stokes stream-function is (Stimson and Jeffery, 1926)

$$\phi^4(\psi) = 0 \quad (3.7)$$

where the components of velocity of the fluid, u , v , in cylindrical coordinates, ρ , z , are

$$u = \frac{1}{\rho} \frac{\partial \psi}{\partial z}, \quad v = -\frac{1}{\rho} \frac{\partial \psi}{\partial \rho} \quad (3.8)$$

and the operator ϕ^2 is defined by

$$\phi^2 = \rho \frac{\partial}{\partial \rho} \left(\frac{1}{\rho} \frac{\partial}{\partial \rho} \right) + \frac{\partial^2}{\partial z^2} \quad (3.9)$$

Using bipolar coordinates, ξ , η , the solution to 3.7 obtained by Stimson and Jeffery is

FIGURE 3.1: System of coordinates for axisymmetrical motion of two spheres

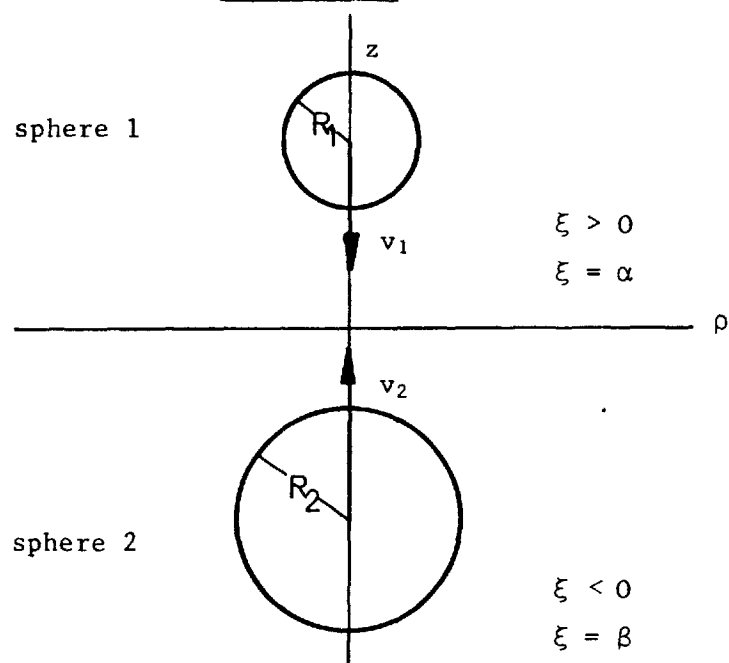
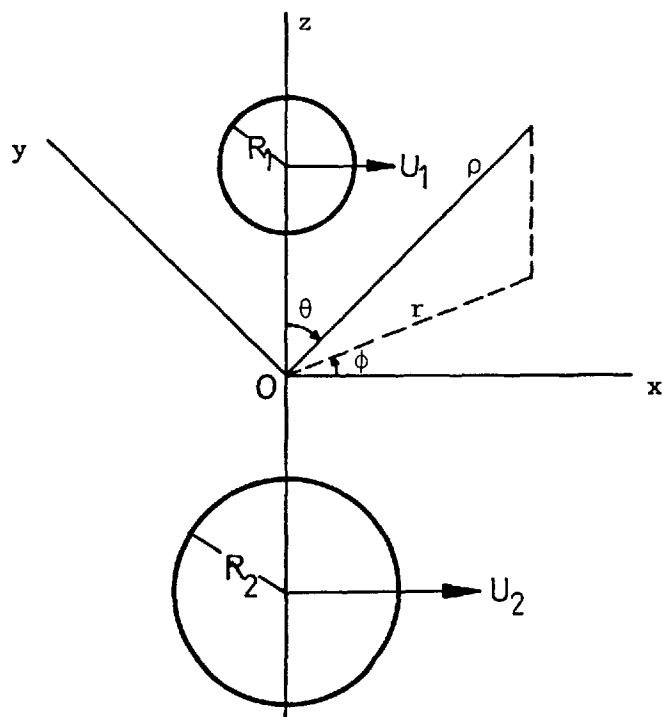


FIGURE 3.2: System of coordinates for asymmetrical motion of two spheres



$$\psi = (\cosh \xi - \mu)^{-3/2} \sum_0^{\infty} U_n V_n \quad (3.10)$$

where V_n is a function related to the Legendre polynomials as follows,

$$V_n = P_{n-1}(\mu) - P_{n+1}(\mu) \quad (3.11)$$

$$\mu = \cos \eta$$

and

$$U_n = A_n \cosh(n-\frac{1}{2}) \xi + B_n \sinh(n-\frac{1}{2}) \xi + C_n \cosh(n+\frac{3}{2}) \xi + D_n \sinh(n+\frac{3}{2}) \xi \quad (3.12)$$

To evaluate the coefficients, A_n , B_n , C_n and D_n , four boundary conditions must be imposed on the spheres.

The boundary conditions in cylindrical coordinates are

On the surface of sphere 1

$$\frac{\partial \psi}{\partial z} = 0 \quad (3.13)$$

$$\frac{\partial \psi}{\partial \rho} = \rho v_1 \quad (3.14)$$

On the surface of sphere 2

$$\frac{\partial \psi}{\partial z} = 0 \quad (3.15)$$

$$\frac{\partial \psi}{\partial \rho} = -\rho v_2 \quad (3.16)$$

These boundary conditions can be easily converted into bipolar coordinates (Appendix 5) and therefore used in equation (3.10).

Substitution of the boundary conditions in equation (3.10) results in a set of four simultaneous equations which contain A_n , B_n , C_n and D_n as unknowns. The equations are as follows,

$$A_n \cosh(n-\frac{1}{2})\alpha + B_n \sinh(n-\frac{1}{2})\alpha + C_n \cosh(n+\frac{3}{2})\alpha + D_n \sinh(n+\frac{3}{2})\alpha =$$

$$\frac{1}{\sqrt{2}} v_1 c^2 \frac{n(n+1)}{2n+1} \left[\frac{e^{-(n-\frac{1}{2})\alpha}}{2n-1} - \frac{e^{-(n+\frac{3}{2})\alpha}}{2n+3} \right] \quad (3.17)$$

$$A_n \cosh(n-\frac{1}{2})\beta + B_n \sinh(n-\frac{1}{2})\beta + C_n \cosh(n+\frac{3}{2})\beta + D_n \sinh(n+\frac{3}{2})\beta =$$

$$- \frac{1}{\sqrt{2}} v_2 c^2 \frac{n(n+1)}{2n+1} \left[\frac{e^{(n-\frac{1}{2})\beta}}{2n-1} - \frac{e^{(n+\frac{3}{2})\beta}}{2n+3} \right] \quad (3.18)$$

$$(n-\frac{1}{2}) \left[A_n \sinh(n-\frac{1}{2})\alpha + B_n \cosh(n-\frac{1}{2})\alpha \right] + (n+\frac{3}{2}) \left[C_n \sinh(n+\frac{3}{2})\alpha \right.$$

$$\left. + D_n \cosh(n+\frac{3}{2})\alpha \right] = - \frac{1}{2\sqrt{2}} v_1 c^2 \frac{n(n+1)}{2n+1} \left[e^{-(n-\frac{1}{2})\alpha} - e^{-(n+\frac{3}{2})\alpha} \right] \quad (3.19)$$

$$(n-\frac{1}{2}) \left[A_n \sinh(n-\frac{1}{2})\beta + B_n \cosh(n-\frac{1}{2})\beta \right] + (n+\frac{3}{2}) \left[C_n \sinh(n+\frac{3}{2})\beta \right.$$

$$\left. + D_n \cosh(n+\frac{3}{2})\beta \right] = - \frac{1}{2\sqrt{2}} v_2 c^2 \frac{n(n+1)}{2n+1} \left[e^{(n-\frac{1}{2})\beta} - e^{(n+\frac{3}{2})\beta} \right] \quad (3.20)$$

In these equations c is the constant of bipolar coordinates and α and β correspond to spheres R_1 and R_2 in bipolar coordinates respectively.

Force on the spheres: The expression for the force exerted by the fluid on a solid sphere has been given by Stimson and Jeffery. It reads

$$F = \pi\mu \int \rho^3 \frac{\partial}{\partial n} \left(\frac{\phi^2(\psi)}{\rho^2} \right) ds \quad (3.21)$$

where n is the direction of the normal drawn outwards from the solid, s is the tangential coordinate and μ is the viscosity of the fluid, and the integral is taken round the meridian section in a direction forming a positive right angle with n .

Replacing ϕ^2 by the corresponding expression in bipolar coordinates, the integration of (3.21) leads to the following expressions for the forces exerted by the fluid on the spheres 1 and 2.

$$F_1 = - \frac{2\sqrt{2} \pi \mu}{c} \sum_{n=1}^{\infty} (2n+1) (A_n + B_n + C_n + D_n), \quad \xi = \alpha \quad (3.22)$$

$$F_2 = - \frac{2\sqrt{2} \pi \mu}{c} \sum_{n=1}^{\infty} (2n+1) (A_n - B_n + C_n - D_n), \quad \xi = \beta \quad (3.23)$$

where A_n , B_n , C_n and D_n can be obtained from equations (3.17)-(3.20).

The correction factors to the force for the two spheres can be subsequently calculated combining equations (3.22) and (3.23) with the equation (3.6).

A subroutine (SUBROUTINE TWOSOL1) was written in order to solve the set of four simultaneous equations (3.17) - (3.20). The method of determinants was employed to solve for the unknowns.

Some results of correction factors, λ , for different ratio of particle sizes, R_1/R_2 , and different dimensionless surface to surface separations, S/R_2 , are presented in Table 3.1. The program was tested against available data in the literature.

In Table 3.2, the results are compared with those of Stimson and Jeffery (1926) for two equal spheres. In Table 3.3, the correction factors for sphere R_1 in a system of two spheres separated by a gap, S/R_2 , of 0.0001 are presented.

The agreement with the values produced by Goren (1970) for two touching spheres is evidently good. Table 3.4 compares the exact results obtained in this work with those of Hestroni and Haber (1978) obtained through the method of reflections. Their results deviate from the exact solution for values of the surface to surface separations below one particle radius.

	S/R_2	λ_1	λ_2
$R_1/R_2 = 1$	.30000000E+02 .20000000E+02 .10000000E+02 .50000000E+01 .20000000E+01 .10000000E+01 .50000000E+00 .50000000E-01 .50000000E-02 .10000000E-02	.95525498E+00 .93626651E+00 .88948753E+00 .82652875E+00 .74225817E+00 .69830409E+00 .67291430E+00 .64801475E+00 .64535662E+00 .64502960E+00	.95525498E+00 .93626651E+00 .88948753E+00 .82652875E+00 .74225817E+00 .69830409E+00 .67291430E+00 .64801475E+00 .64535662E+00 .64502960E+00
$R_1/R_2 = 0.1$	.30000000E+02 .20000000E+02 .10000000E+02 .50000000E+01 .20000000E+01 .10000000E+01 .50000000E+00 .50000000E-01 .50000000E-02 .10000000E-02	.95200697E+00 .92943448E+00 .86682991E+00 .76105059E+00 .54734838E+00 .36401123E+00 .21576235E+00 .52355218E-01 .37892130E-01 .36669478E-01	.99540992E+00 .99339766E+00 .98831830E+00 .98145736E+00 .97447444E+00 .97609133E+00 .98262241E+00 .99496925E+00 .99616245E+00 .99603431E+00
$R_1/R_2 = 0.05$	.30000000E+02 .20000000E+02 .10000000E+02 .50000000E+01 .20000000E+01 .10000000E+01 .50000000E+00 .50000000E-01 .50000000E-02 .10000000E-02	.95181875E+00 .92903124E+00 .86542824E+00 .75672060E+00 .53308188E+00 .33832408E+00 .18122085E+00 .21906101E-01 .11446934E-01 .10649291E-01	.99770171E+00 .99669241E+00 .99414213E+00 .99070502E+00 .98736630E+00 .98861895E+00 .99246881E+00 .99886525E+00 .99917936E+00 .99888207E+00
$R_1/R_2 = 0.02$	.30000000E+02 .20000000E+02 .10000000E+02 .50000000E+01 .20000000E+01 .10000000E+01 .50000000E+00 .50000000E-01 .50000000E-02 .10000000E-02	.95170541E+00 .92878806E+00 .86458064E+00 .75408621E+00 .52437711E+00 .32282537E+00 .16111130E+00 .89028146E-02 .23072555E-02 .19172508E-02	.99907990E+00 .99867542E+00 .99765277E+00 .99627657E+00 .99498140E+00 .99559497E+00 .99727372E+00 .99974471E+00 .99956251E+00 .99902917E+00

TABLE 3.1: Correction factors for motion of two spheres along their line of centres.

α	S/R_1	λ_1	λ_1 (Stimson & Jeffery)
0.5	0.2552	.6596346392	0.663
1	1.0862	.7024523598	0.702
1.5	2.7048	.7677791471	0.768
2	5.5244	.8362749747	0.836
2.5	10.2646	.8915852675	0.892
3	18.1353	.9307947304	0.931
∞	∞	1	1.000

TABLE 3.2: Correction factors for motion of two equal spheres approaching each other along their line of centres.

R_1/R_2	λ_1	λ_1 (Goren)
0.05	.104731E-01	0.0105
0.1	.363960E-01	0.0364
0.25	.155422E+00	0.155
0.5	.364737E+00	0.365
1	.644564E+00	0.645
2	.865243E+00	0.866
4	.964176E+00	0.965
10	.991915E+00	0.997

TABLE 3.3: Correction factors for axisymmetric flow of two almost touching spheres.

$$S/R_2 = 0.0001$$

S/R_2	λ_1	λ_2
.30000000E+02	.95200697E+00	.99540992E+00
.20000000E+02	.92943448E+00	.99339766E+00
.10000000E+02	.86682991E+00	.98831830E+00
.50000000E+01	.76105059E+00	.98145736E+00
.20000000E+01	.54734838E+00	.97447444E+00
.10000000E+01	.36401123E+00	.97609133E+00
.50000000E+00	.21576235E+00	.98262241E+00
.50000000E-01	.52355218E-01	.99496925E+00
.50000000E-02	.37892130E-01	.99616245E+00
.10000000E-02	.36669478E-01	.99603431E+00
S/R_2	λ_1 (Haber)	λ_2 (Haber)
.30000000E+02	.95200697E+00	.99540961E+00
.20000000E+02	.92943453E+00	.99339615E+00
.10000000E+02	.86683135E+00	.98829872E+00
.50000000E+01	.76107889E+00	.98124357E+00
.20000000E+01	.54810042E+00	.97128815E+00
.10000000E+01	.36876224E+00	.96098076E+00
.50000000E+00	.23265457E+00	.93763351E+00
.50000000E-01	.13093507E+00	.82365343E+00
.50000000E-02	.13280298E+00	.79457368E+00
.10000000E-02	.13322776E+00	.79166564E+00

TABLE 3.4: Comparison of exact and approximate solutions for motion along the line of centres.

$$R_1/R_2 = 0.1$$

3.2.2 Motion of Two Spheres Perpendicular to their Line of Centres

In this section, the approach used by Wakiya has been adopted. His approach provides a general solution for the flow field due to the motion of two spheres perpendicular to their line of centres, Figure 3.2. The force exerted on either of the spheres can consequently be evaluated. The equations of motion (3.3), in cylindrical coordinates (r, ϕ, z) , are as follows,

$$\frac{1}{\mu} \frac{\partial P}{\partial r} = (\nabla^2 - \frac{1}{r^2}) v_r - \frac{2}{r^2} \frac{\partial v_\phi}{\partial \phi} \quad (3.24.1)$$

$$\frac{1}{\mu} \frac{\partial P}{r \partial \phi} = (\nabla^2 - \frac{1}{r^2}) v_\phi + \frac{2}{r^2} \frac{\partial v_r}{\partial \phi} \quad (3.24.2)$$

$$\frac{1}{\mu} \frac{\partial P}{\partial z} = \nabla^2 v_z \quad (3.24.3)$$

$$\nabla^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial^2}{\partial \phi^2} + \frac{\partial^2}{\partial z^2}$$

and the continuity equation (3.4), is given as

$$\left(\frac{\partial}{\partial r} + \frac{1}{r} \right) v_r + \frac{\partial v_\phi}{r \partial \phi} + \frac{\partial v_z}{\partial z} = 0 \quad (3.24.4)$$

where v_r , v_ϕ , v_z are the components of the velocity of the fluid, P is the pressure and μ is the fluid viscosity. Solutions of equation (3.24) having a plane symmetry are

$$v_r = \frac{1}{2} \sum_{m=0}^{\infty} \left(\frac{r}{c} q_m + u_m + v_m \right) \cos m\phi \quad (3.25.1)$$

$$v_\phi = \frac{1}{2} \sum_{m=0}^{\infty} (u_m - v_m) \sin m\phi \quad (3.25.2)$$

$$v_z = \frac{1}{2} \sum_{m=0}^{\infty} \left(\frac{z}{c} q_m + 2 w_m \right) \cos m\phi \quad (3.25.3)$$

$$P = \frac{\mu}{c} \sum_{m=0}^{\infty} q_m \cos m\phi \quad (3.25.4)$$

where c is the constant length of bipolar coordinate system and q_m , v_m , u_m and w_m are function of r , z which satisfy

$$L_m^2 q_m = L_m^2 w_m = L_{m-1}^2 v_m = L_{m+1}^2 u_m = 0 \quad (3.26)$$

where the operator L^2 is given by

$$L_\ell^2 = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} - \frac{\ell^2}{r^2} + \frac{\partial^2}{\partial z^2} \quad (\ell = m-1, m, m+1) \quad (3.27)$$

The equation of continuity imposes the relation,

$$(z+r \frac{\partial}{\partial r} + z \frac{\partial}{\partial z}) q_m + c \left[\left(\frac{\partial}{\partial r} + \frac{m+1}{r} \right) u_m + \left(\frac{\partial}{\partial r} - \frac{m-1}{r} \right) v_m + 2 \frac{\partial w_m}{\partial z} \right] = 0 \quad (3.28)$$

Converting the system of coordinates to bipolar, for equations (3.26) to be satisfied, the expressions for u_m, v_m, q_m and w_m should be as follows,

$$w_m = (\cosh \xi - t)^{\frac{1}{2}} \sum_{n=m}^{\infty} \left[A_n^m \sinh(n+\frac{1}{2}) \xi + B_n^m \cosh(n+\frac{1}{2}) \xi \right] P_n^m(t) \quad (3.29.1)$$

$$q_m = (\cosh \xi - t)^{\frac{1}{2}} \sum_{n=m}^{\infty} \left[C_n^m \cosh(n+\frac{1}{2}) \xi + D_n^m \sinh(n+\frac{1}{2}) \xi \right] P_n^m(t) \quad (3.29.2)$$

$$v_m = (\cosh \xi - t)^{\frac{1}{2}} \sum_{n=m-1}^{\infty} \left[E_n^m \cosh(n+\frac{1}{2}) \xi + F_n^m \sinh(n+\frac{1}{2}) \xi \right] P_n^{m-1}(t) \quad (3.29.3)$$

$$u_m = (\cosh \xi - t)^{\frac{1}{2}} \sum_{n=m+1}^{\infty} \left[G_n^m \cosh(n+\frac{1}{2}) \xi + H_n^m \sinh(n+\frac{1}{2}) \xi \right] P_n^{m+1}(t) \quad (3.29.4)$$

where $t = \cos \eta$ and $P_n^m(t)$ is the associated Legendre polynomial of order n and rank m .

$$P_n^m(t) = \frac{(1-t^2)^{m/2}}{n! 2^n} \frac{d^{n+m}}{dt^{n+m}} (t^2 - 1)^n \quad (3.30)$$

Also, in order that (3.29.1) to (3.29.4) satisfy the continuity equation (3.28), two sets of relations are needed between the constants. These are found to be

$$5C_n^m - (n-m)C_{n-1}^m + (n+m+1)C_{n+1}^m + 2E_{n-1}^m - E_{n-1}^m - E_{n+1}^m - 2(n-m)(n+m+1)G_n^m + \\ (n-m-1)(n-m)G_{n-1}^m + (n+m+1)(n+m+2)G_{n+1}^m + 2(2n+1)A_n^m - 2(n-m)A_{n-1}^m - 2(n+m+1)A_{n+1}^m = 0 \quad (3.31.1)$$

$$\begin{aligned}
& 5D_n^m - (n-m) D_{n-1}^m + (n+m+1) D_{n+1}^m + 2F_n^m - F_{n-1}^m - F_{n+1}^m - 2(n-m)(n+m+1) H_n^m + \\
& (n-m-1)(n-m) H_{n-1}^m + (n+m+1)(n+m+2) H_{n+1}^m + 2(2n+1) B_n^m - 2(n-m) B_{n-1}^m - \\
& 2(n+m+1) B_{n+1}^m = 0
\end{aligned} \tag{3.31.2}$$

Due to the symmetry of the system about the sphere's centreline m can be taken equal to 1.

To evaluate the fluid velocity components, the constants appearing in the equations of motion and continuity are required. These constants can be obtained using the following boundary conditions.

$$\text{On sphere 1} \quad v_r = U_1 \cos \phi \tag{3.32}$$

$$v_\phi = -U_1 \sin \phi \tag{3.33}$$

$$v_z = 0 \tag{3.34}$$

$$\text{On sphere 2} \quad v_r = U_2 \cos \phi \tag{3.35}$$

$$v_\phi = -U_2 \sin \phi \tag{3.36}$$

$$v_z = 0. \tag{3.37}$$

These boundary conditions are then written in terms of u, v, q, w , which are in turn replaced by equations (3.29). After some algebraic manipulations (Appendix 6) the following equations were obtained.

$$\begin{aligned}
& C_n \cosh(n+\frac{1}{2}) \xi + D_n \sinh(n+\frac{1}{2}) \xi = \frac{2}{\sinh \xi} \frac{n+2}{2n+3} \left[A_{n+1} \sinh(n+\frac{3}{2}) \xi \right. \\
& \left. + B_{n+1} \cosh(n+\frac{3}{2}) \xi \right] - 2 \coth \xi \left[A_n \sinh(n+\frac{1}{2}) \xi + B_n \cosh(n+\frac{1}{2}) \xi \right] \\
& + \frac{2}{\sinh \xi} \frac{n-1}{2n-1} \left[A_{n-1} \sinh(n-\frac{1}{2}) \xi + B_{n-1} \cosh(n-\frac{1}{2}) \xi \right]
\end{aligned} \tag{3.38}$$

$$\begin{aligned}
E_n \cosh(n+\frac{1}{2}) \xi + F_n \sinh(n+\frac{1}{2}) \xi &= \frac{1}{\sinh \xi} \left\{ \frac{(n+1)(n+2)}{2n+3} \left[A_{n+1} \sinh(n+\frac{3}{2}) \xi \right. \right. \\
&+ \left. B_{n+1} \cosh(n+\frac{3}{2}) \xi \right] - \left[A_{n-1} \sinh(n-\frac{1}{2}) \xi + B_{n-1} \cosh(n-\frac{1}{2}) \xi \right] \frac{n(n-1)}{2n-1} \left. \right\} \\
&+ 2\sqrt{2} U e^{-(n+\frac{1}{2}) \xi}
\end{aligned} \tag{3.39}$$

$$\begin{aligned}
G_n \cosh(n+\frac{1}{2}) \xi + H_n \sinh(n+\frac{1}{2}) \xi &= \frac{1}{\sinh \xi} \left\{ -\frac{1}{2n+3} \left[A_{n+1} \sinh(n+\frac{3}{2}) \xi \right. \right. \\
&+ \left. B_{n+1} \cosh(n+\frac{3}{2}) \xi \right] + \frac{1}{2n-1} \left[A_{n-1} \sinh(n-\frac{1}{2}) \xi + B_{n-1} \cosh(n-\frac{1}{2}) \xi \right] \left. \right\}
\end{aligned} \tag{3.40}$$

Setting $\xi = \xi_1$, $U = U_1$ and $\xi = -\xi_2$, $U = U_2$ to any of the equations above, leads into six different relations amongst the constants. These equations, together with the two continuity equations, provide the basis for the evaluation of the unknowns.

The Force on the Spheres

The expressions for the force exerted by the fluid on the spheres are also obtained by Wakiya and are given below.

$$\text{On sphere 1} \quad F_1 = -6\pi \mu R_1 \left(\frac{\sqrt{2}}{3} \right) \sinh \xi_1 \sum_{n=0}^{\infty} (E_n + F_n) \tag{3.41}$$

$$= -6\pi \mu R_1 \left(\frac{\sqrt{2}}{3} \right) \sinh \xi_1 \sum_{n=0}^{\infty} n(n+1) (C_n + D_n) \tag{3.42}$$

$$\text{On sphere 2} \quad F = -6\pi \mu R_2 (\sqrt{2}/3) \sinh |\xi_2| \sum_{n=0}^{\infty} (E_n - F_n) \tag{3.43}$$

$$= -6\pi \mu R_2 (\sqrt{2}/3) \sinh |\xi_2| \sum_{n=0}^{\infty} n(n+1) (C_n - D_n) \tag{3.44}$$

In order to find the correction factors, these equations are combined with equation (3.6). The problem then reduces to finding the constants in the force expressions.

Numerical Solution

Considering equations (3.38)-(3.40), C_n , D_n , E_n , F_n , G_n and H_n can be written as functions of A_{n+2} , A_{n+1} , A_n , A_{n-1} , A_{n-2} , B_{n+2} , B_{n+1} , B_n , B_{n-1} , B_{n-2} . Use of these relations in the continuity equations (3.31) results into two expressions which are only functions of A's and B's. These expressions obtained after tedious mathematical manipulations are as follows.

$$A_{11}A_{n+1} + A_{01}A_n + AA_1 A_{n-1} + B_{11} B_{n+1} + B_{01} B_n + BB_1 B_{n-1} + \text{CONS1} = 0 \quad (3.45.1)$$

$$A_{22}A_{n+1} + A_{02}A_n + AA_2 A_{n-1} + B_{22}B_{n+1} + B_{02}B_n + BB_2 B_{n-1} + \text{CONS2} = 0 \quad (3.45.2)$$

The coefficients for A_{n+2} , B_{n+2} , A_{n-2} , B_{n-2} were found to be zero. The rest of the coefficients are given in Appendix 7.

For any n , two equations containing A's and B's are available, namely, equations (3.45). In order to solve the $2n$ equations for the $(2n+2)$ unknowns, $A_1 \dots A_{n+1}$, $B_1 \dots B_{n+1}$, a value for n was chosen in such a way that A_{n+1} and B_{n+1} could be assumed to be zero. By expressing A_n and B_n as a function of A_{n-1} and B_{n-1} and replacing these in the successive equations for decreasing n , the last two equations, for $n=1$, contain only A_1 and B_1 which can then be calculated and back substituted in the other equations in order to obtain A_2 , B_2 , etc.

To reduce the computer memory needed to process the program, the dimension of the matrix containing the coefficients in equations (3.45) had to be contracted to a band matrix of breadth 7. Numerical solution of such a system of linear equations can then be achieved by Gaussian elimination method. A subroutine (SUBROUTINE AB) was written to calculate the coefficients in equations (3.45). This routine also arranges the coefficients into a band matrix as described

above. The Gaussian elimination is carried out by subroutine GAUSS2 which finds the A's and B's. These values are then used in subroutine TWOSOL2 to obtain the correction factors for the force on the spheres. .

The convergence of the results is checked in this program and if the desired accuracy has not been achieved, the value of n is increased. The procedure followed for the calculation of the coefficients and consequently A's and B's is very time consuming. Therefore, whenever the accuracy has not been achieved and the number of iterations should be increased, the program stores all the old values of coefficients A's and B's up to n , and only new values are calculated.

Table 3.5 shows the correction factors produced by this program for different dimensionless surface to surface distances (S/R_2), and for several particle size ratios, R_1/R_2 .

To check whether the program was working correctly, results obtained were compared with data available in the literature. Table 3.6 compares data produced by Goldman, Cox and Brenner (1966), for two equal spheres with those of this work. Also Table 3.7 compares the results with those of O'Neil and Majumdar for two unequal spheres. Comparison with Haber's results for unequal spheres based on the method of reflections is also made in Table 3.8. Again, as in the case of the motion of two spheres along their line of centres, the method of reflections deviates from the exact solution for separations below one sphere radius.

As the gap between the two spheres approaches zero, the convergence of the numerical solution for both motion along and perpendicular to the lines of centres becomes poor.

It is important to mention that as two spheres come very close to each other, a highly sheared region is created. The exact solution of the linearised Navier-Stokes equations is not a uniformly valid

approximate solution of the full Navier-Stokes equations in this region for the neglected inertia terms are comparable with the viscous terms.

	S/R_2	λ_1	λ_2
$R_1/R_2 = 1$	.30000000E+02 .20000000E+02 .10000000E+02 .50000000E+01 .20000000E+01 .10000000E+01 .50000000E+00 .50000000E-01	.97708535E+00 .96699206E+00 .94095256E+00 .90229945E+00 .83882616E+00 .79492590E+00 .76378577E+00 .72896533E+00	.97708535E+00 .96699206E+00 .94095256E+00 .90229945E+00 .83882616E+00 .79492590E+00 .76378577E+00 .72896533E+00
$R_1/R_2 = 0.1$	.30000000E+02 .20000000E+02 .10000000E+02 .50000000E+01 .20000000E+01 .10000000E+01 .50000000E+00 .50000000E-01	.97593273E+00 .96455051E+00 .93268060E+00 .87733644E+00 .75503556E+00 .62829324E+00 .49419529E+00 .24658838E+00	.99764565E+00 .99656891E+00 .99368093E+00 .98911602E+00 .98110117E+00 .97588846E+00 .97392353E+00 .98052835E+00
$R_1/R_2 = 0.05$	.30000000E+02 .20000000E+02 .10000000E+02 .50000000E+01 .20000000E+01 .10000000E+01 .50000000E+00 .50000000E-01	.97586557E+00 .96440517E+00 .93215920E+00 .87561192E+00 .74807164E+00 .61170327E+00 .46191099E+00 .16645850E+00	.99882101E+00 .99828064E+00 .99682791E+00 .99452317E+00 .99047309E+00 .98792625E+00 .98729063E+00 .99294400E+00
$R_1/R_2 = 0.02$	.30000000E+02 .20000000E+02 .10000000E+02 .50000000E+01 .20000000E+01 .10000000E+01 .50000000E+00 .50000000E-01	.97582510E+00 .96431743E+00 .93184280E+00 .87455581E+00 .74371881E+00 .60110294E+00 .44078137E+00 .11024543E+00	.99952797E+00 .99931134E+00 .99872813E+00 .99780083E+00 .99617104E+00 .99517197E+00 .99502382E+00 .99810749E+00

TABLE 3.5: Correction factors for motion of two spheres perpendicular to their line of centres.

α	λ	λ (Goldman, Cox & Brenner)
∞	.10000000E+01	1
5.000	.99497203E+00	0.99497
4.000	.98645099E+00	0.98645
3.000	.96403695E+00	0.96404
2.500	.94216139E+00	0.94216
2.000	.90858713E+00	0.90859
1.750	.88630533E+00	0.88631
1.500	.86014912E+00	0.86015
1.250	.83067797E+00	0.83068
1.000	.79956888E+00	0.79957
.800	.77554185E+00	0.77554
.500	.74566588E+00	0.74565
.300	.73237046E+00	0.73235
.100	.72558161E+00	0.72552
.070	.72516865E+00	0.72509

TABLE 3.6: Comparison of the results for motion perpendicular to the line of centres for two equal spheres.

S/R_2	λ_1	λ_2	λ_1 (Majumdar)	λ_2 (Majumdar)
.10000000E+02	.93660149E+00	.96936763E+00	0.9366	0.9694
.50000000E+01	.88970480E+00	.94821488E+00	0.8897	0.9482
.10000000E+01	.72501267E+00	.88626275E+00	0.7250	0.8863
.10000000E+00	.58731887E+00	.85394187E+00	0.5873	0.8540
.10000000E-01	.56646739E+00	.85124344E+00	0.5664	0.8512
.50000000E-02	.56525550E+00	.85113591E+00	0.5653	0.8510
.10000000E-02	.56428058E+00	.85116987E+00	0.5643	0.8509

TABLE 3.7: Comparison of results for motion perpendicular to the line of centres for two unequal spheres.

$$R_1/R_2 = 0.5.$$

S/R_2	λ_1	λ_2
.30000000E+02	.97593273E+00	.99764565E+00
.20000000E+02	.96455051E+00	.99656891E+00
.10000000E+02	.93268060E+00	.99368093E+00
.50000000E+01	.87733644E+00	.98911602E+00
.20000000E+01	.75503558E+00	.98110117E+00
.10000000E+01	.62829324E+00	.97588846E+00
.50000000E+00	.49419529E+00	.97392353E+00
.50000000E-01	.24658838E+00	.98052835E+00
.50000000E-02	.20855879E+00	.98290120E+00
S/R_2	λ_1 (Haber)	λ_2 (Haber)
.30000000E+02	.97593273E+00	.99764565E+00
.20000000E+02	.96455051E+00	.99656891E+00
.10000000E+02	.93268054E+00	.99368093E+00
.50000000E+01	.87733433E+00	.98911576E+00
.20000000E+01	.75492669E+00	.98108749E+00
.10000000E+01	.62726611E+00	.97575829E+00
.50000000E+00	.48927570E+00	.97350885E+00
.50000000E-01	.21233300E+00	.97677153E+00
.50000000E-02	.16496557E+00	.97820386E+00

TABLE 3.8: Comparison of exact and approximate solutions for motion perpendicular to the line of centres.

$$R_1/R_2 = 0.1$$

3.3 Intermolecular Forces

3.3.1 Disjoining Pressure

During the process of flotation, for effective capture of a particle by a bubble to occur, the intervening film of liquid between both has to thin and eventually rupture.

The forces in thin films can be treated as intermolecular attractions of the London/van der Waals type, electrostatic effects which generally lead to repulsive forces and lastly, the influence of the surface itself on these forces. All of these come into effect only when the liquid layer separating the particles has thinned down to typically a fraction of a micron.

Derjaguin (1939) evolved the concept of "disjoining pressure" to describe the process of thinning, which is defined as the derivative of the free energy of the system with respect to film thickness per unit area taken with negative sign.

For wetting films on solid substrates it has been shown (Read and Kitchener, 1967) that the film behaved as though it possessed an excess pressure, Π , acting normal to the surface and resisting further thinning. The disjoining pressure is measured by the difference in pressure between a bubble pressed against a solid substrate and the pressure in the liquid in the neighbourhood of the solid film interface.

In general, this pressure is made up of several components, a London/van der Waals term (Π_{VW}), an electrical double layer contribution (Π_{DL}) and a term called "specific surface term", which accounts for the hydrophobic or hydrophilic nature of the substrate (Π_{S}).

Thus

$$\Pi(h) = \Pi_{\text{VW}}(h) + \Pi_{\text{DL}}(h) + \Pi_{\text{S}}(h)$$

where h = film thickness.

Measurement of the thickness of equilibrium wetting films and its change with electrolyte concentration for films of dilute aqueous solutions formed between captive gas bubbles and a silica plate (Read and Kitchener, 1967, 1969) showed that for film thickness greater than $300 \text{ \AA}$, the predominant component of the disjoining pressure is the double layer force. They showed that the London/van der Waals forces were negligible and suggested that more specific interactions, such as hydrogen bonding, were unimportant at those thicknesses.

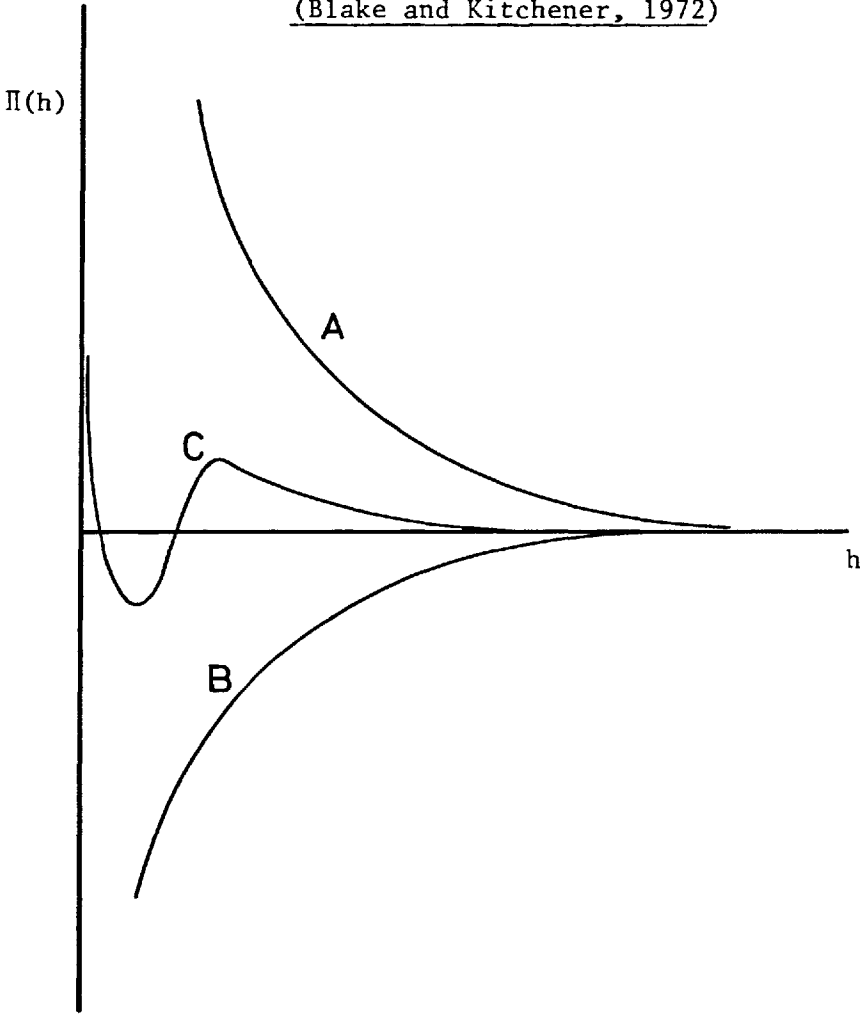
At very small distances, the other contributions become important as it is believed that hydrogen bond formation between the surface and the water molecules is the reason for the silica hydrophilicity.

By methylating the surface of silica (Blake and Kitchener, 1972), the surface was rendered hydrophobic. In such a case, aqueous films formed on the surface were expected to be unstable. But measurement of zeta potentials of both clean and methylated surfaces indicated almost the same value for both of them. This was suggested to be the reason for stability of the film when the thickness of the film was thick. At smaller thicknesses, however, the effect of hydrophobicity of the surface was supposed to come into action resulting in the rupture of the film.

Figure 3.3 shows the dependence of Π upon the film thickness, h . Curves A, B represent a stable ($\frac{\partial \Pi}{\partial h} < 0$), and an unstable system ($\frac{\partial \Pi}{\partial h} > 0$), respectively. Curve C corresponds to the case of a hydrophobic surface where thicknesses to the right of the maximum would be metastable and those to the left of the maximum would be unstable.

Although the magnitude of the surface forces cannot still be obtained, according to Blake and Kitchener (1972) there is little

FIGURE 3.3: Variation of disjoining pressure
versus film thickness
(Blake and Kitchener, 1972)



doubt that their range of action is distinctly smaller than the range of the electrical double layer.

In the next part of this chapter, the terms contributing to the disjoining pressure will be studied.

In Section 3.3.2, the electrical double layer is discussed in detail and in 3.3.3 the London/van der Waals forces will be described. Also, the surface of the particle will be considered so hydrophobic that the specific term $\Pi_s(h)$ will be taken as zero.

3.3.2 Electrical Phenomena

The phenomena involved with electricity and tangential movement of two phases along each other are named the electrokinetic phenomena. These phenomena may arise either from an external electric field directed along the phase boundary and resulting in a movement, or from a movement of the phases along each other, resulting in a transport of electricity. Examples of the first kind are electro-osmosis and electrophoresis and of the second kind are streaming potential and migration potential.

It has been known that the movement of the liquid does not begin immediately next to the wall, but that a layer of the liquid with a thickness of one molecule or a few molecules is stationary with respect to the wall.

It is also thought that the electrical potential in the slipping plane between the fixed and the flowing liquid is the one that determines the electrokinetic phenomena. This potential is usually called the zeta potential.

3.3.2.1 The Electrical Double Layer

In general, the surface of a material when brought into contact with an aqueous medium acquires a net surface electric charge, the

possible charging mechanism being ionisation, ion adsorption and ion dissolution.

This surface charge influences the distribution of ions in the polar medium; a neutralising excess of counter ions over co-ions in the vicinity of the surface and also distributed in a diffuse manner in the medium maintains electroneutrality. The charged surface and its diffuse ionic layer constitute what has been termed the electrical double layer.

The theoretical treatment of the double layer at a plane interface was given first by Gouy and Chapman (Gouy, 1910; Chapman, 1913). They suggested that the electrical double layer consists of excess ions or electrons present on the solid phase and an equivalent amount of ionic charge of opposite sign distributed in the liquid phase near the interface (diffused part). The space charge in the solution side was supposed to consist of unequal distribution of point-like ions.

The diffused model of Gouy-Chapman proved to be too oversimplifying, as the model predicted an unrealistically high electrolyte concentration near the interface when the solution was rather concentrated with electrolyte. This behaviour was attributed to the neglecting of the ionic dimensions.

The influence of the dimensions of these ions is greatest near the wall and an important correction into the double layer theory could be made by assuming finite dimensions for only the ions of the first layer adjacent to the wall; or, in other words, assuming that these ions approach the wall to a distance smaller than a few $\text{\AA}$. With this approach, concentrations and potentials in the double layer drop already to values low enough to warrant the approximation of the ions as point charges. This now reduces to the application

of the Gouy-Chapman theory with the first layer of ions not immediately at the wall but at a distance, δ , away from it. This major correction was first proposed by Stern (1924).

Stern assumed that a region of firmly bound ions existed right next to the surface, and the centres of these ions could not approach closer to the surface than half an ionic diameter. According to Stern's theory, the potential drop, ψ_0 , over the double layer is divided into a potential, ψ_δ , over the diffuse part of the double layer and $\psi_0 - \psi_\delta$ over the rigid part, Figure 3.4. The Gouy-Chapman model can then be applied, except for the fact that the diffuse layer does not reach to the wall but only to a distance, δ , from it.

At some distance from the surface the ions change from being firmly bound to being free to move in the liquid. A plane of shear is assumed to exist at this distance from the surface. This plane is thought to be a region of rapidly changing viscosity rather than a true plane. The potential at the plane of shear is called the "zeta potential" and is the potential which manifests itself in electrokinetic phenomena.

3.3.2.2 Distribution of Potential in the Double Layer

In the Gouy-Chapman model for the diffuse part of the double layer, the Coulomb interaction between the charges present in the system is described by the Poisson equation (Kruyt, 1952).

$$\nabla^2 \psi = - \frac{4\pi\rho}{\epsilon} \quad (3.46)$$

where ϵ is the dielectric constant of the medium and ρ is the space charge density.

The distribution of the ions is governed by the Boltzmann relation

FIGURE 3.4: The physical presentation of an electric double layer according to Stern's theory (Shaw, 1969)

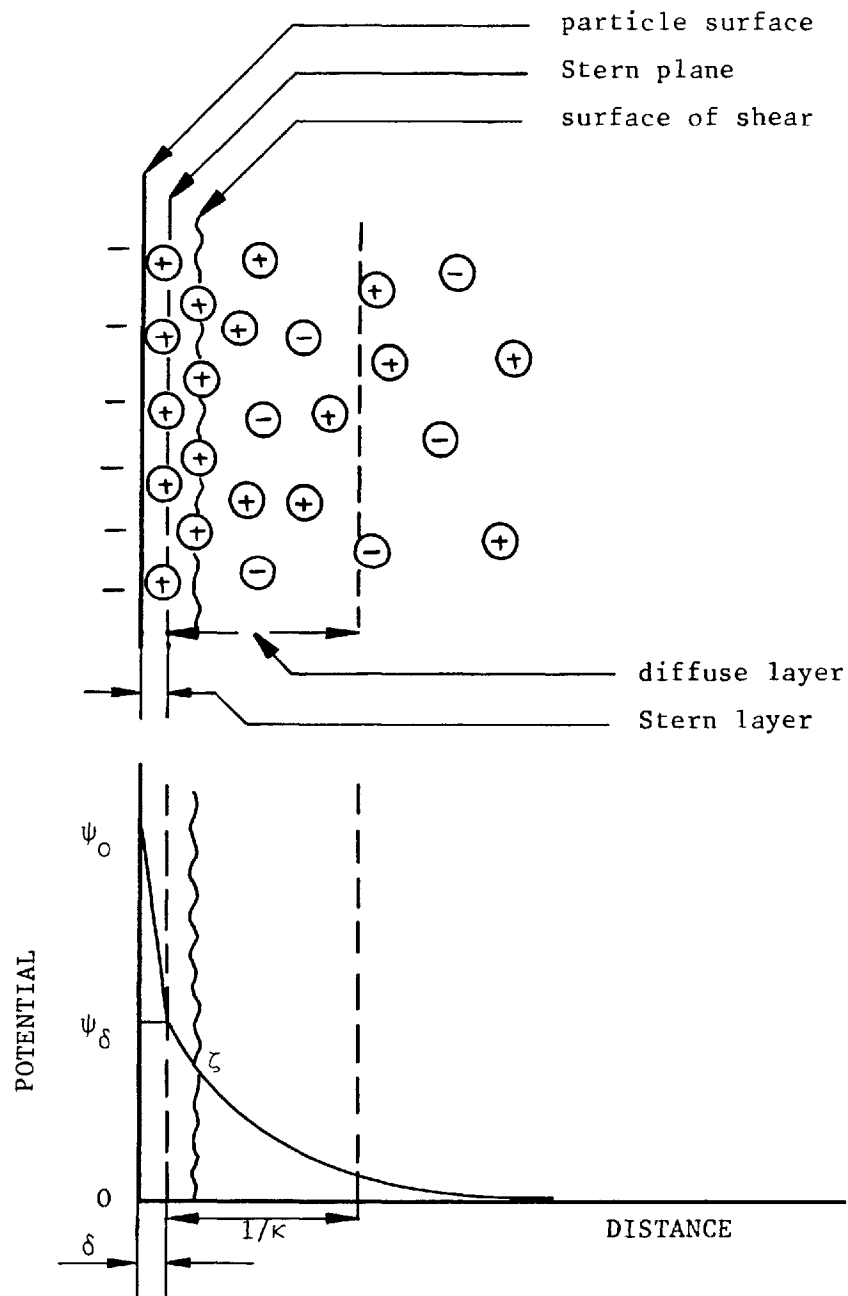
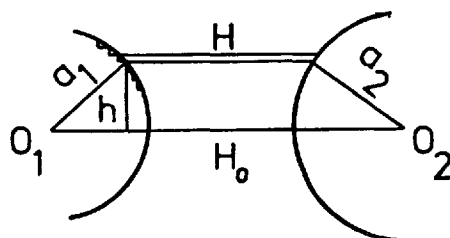


FIGURE 3.5: The geometric presentation of Derjaguin method for calculation of repulsion forces (Kruyt, 1952)



$$n_i = n_{i0} \exp (- z_i e \psi / K T) \quad (3.47)$$

n_i is the concentration of ions of kind i , n_{i0} is its concentration in the bulk of solution, z_i is the valency of the ion, K is the Boltzmann constant, T is the absolute temperature and e is the electronic charge.

The space charge density is given by

$$\rho = \sum z_i e n_i \quad (3.48)$$

Combining these equations, the following relation results

$$\nabla^2 \psi = - \frac{4\pi}{\epsilon} \sum z_i e n_{i0} \exp (- z_i e \psi / K T) \quad (3.49)$$

Simplifying the above expression for small potentials, ($\psi < 25$ mV, Debye-Hückel approximation) this equation is converted to

$$\nabla^2 \psi = \kappa^2 \psi \quad (3.50)$$

where κ is the Debye-Hückel reciprocal length parameter and is given by

$$\kappa^2 = \frac{4\pi e^2 \sum n_{i0} z_i^2}{\epsilon K T} \quad (3.51)$$

For an infinite flat plate, equation (3.50) can be expressed in Cartesian coordinates as

$$\frac{d^2 \psi}{dx^2} = \kappa^2 \psi \quad (3.52)$$

which after integration renders

$$\psi = A_1 \cosh \kappa x + A_2 \sinh \kappa x \quad (3.53)$$

where A_1 and A_2 are constants to be evaluated.

When two parallel surfaces, each bearing a double layer, approach each other to a distance where the two diffuse double layers begin to

interact, again the same procedure as above could be used to describe the potential between the two surfaces. The only difference with the case of a single double layer are now the boundary conditions to apply. In the case of a single double layer, the potential and its derivative are zero far away from the wall and the potential at the wall ($x = 0$) is known. For the case of two dissimilar plates a distance $2d$ apart, equation (3.53) must satisfy the following boundary conditions,

$$\begin{aligned} \text{at } x = 0 & \quad \psi = \psi_{01} \\ \text{at } x = 2d & \quad \psi = \psi_{02} \end{aligned}$$

where ψ_{01} and ψ_{02} are the total double layer potentials (surface potentials) of the plates. Applying these boundary conditions, equation (3.53) leads to

$$\psi = \psi_{01} \cosh \kappa x + \left(\frac{\psi_{02} - \psi_{01} \cosh 2\kappa d}{\sinh 2\kappa d} \right) \sinh \kappa x \quad (3.54)$$

where

$$\kappa = \sqrt{\frac{4\pi e^2}{\epsilon K T} \sum (n_i z_i^2)}$$

This equation describes the distribution of potential as a function of distance between surfaces of ψ_{01} and ψ_{02} .

3.3.2.3 Potential Energy of Interaction between Two Flat Surfaces

The potential energy, V_I , of interaction between two double layers is equal to the change in free energy of the double layer system when the plates are brought close to each other from infinity.

$$V_I = \Delta G = G_{2d} - G_{\infty} \quad (3.55)$$

where G_{2d} and G_{∞} are the free energies of the double layer systems when

the plates are separated by distances of $2d$ and infinity, respectively. For constant and small surface potentials (Verwey and Overbeek, 1948), the free energy of a single double layer is given by

$$G = -\frac{1}{2} \sigma \psi_0 \quad (3.56)$$

where σ is the surface charge density. Thus, G_{2d} , the free energy of the double layer system, is equal to the sum of the free energies of the separate double layers,

$$G_{2d} = -\frac{1}{2} (\sigma_1 \psi_{01} + \sigma_2 \psi_{02}) \quad (3.57)$$

where σ_1 and σ_2 are the surface charge densities of the separate double layers.

The surface charge density at a plane surface as given by Kruyt (1952) is

$$\sigma = -\frac{\epsilon}{4\pi} \left(\frac{\partial \psi}{\partial x} \right)_{x=0} \quad (3.58)$$

Use of equation (3.54) in this expression gives

$$\begin{aligned} \sigma_1 &= -\frac{\epsilon K}{4\pi} (\psi_{02} \operatorname{cosech} 2\kappa d - \psi_{01} \coth 2\kappa d) \\ \sigma_2 &= \frac{\epsilon K}{4\pi} (\psi_{02} \coth 2\kappa d - \psi_{01} \operatorname{cosech} 2\kappa d) \end{aligned} \quad (3.59)$$

Substituting for σ_1 and σ_2 in equation (3.57)

$$G_{2d} = \frac{\epsilon K}{8\pi} \left[2\psi_{01} \psi_{02} \operatorname{cosech} 2\kappa d - (\psi_{01}^2 + \psi_{02}^2) \coth 2\kappa d \right] \quad (3.60)$$

At large separation of the plates,

$$G_{\infty} = -\frac{\epsilon K}{8\pi} (\psi_{01}^2 + \psi_{02}^2) \quad (3.61)$$

Applying these into equation (3.55),

$$V_I = \frac{\epsilon K}{8\pi} \left[(\psi_{01}^2 - \psi_{02}^2)(1 - \coth 2kd) + 2\psi_{01} \psi_{02} \operatorname{cosech} 2kd \right] \quad (3.62)$$

This expression gives the potential energy of interaction of two parallel, infinite, flat double layers as a function of the surface potential of each plate, and the separation of the plates (Hogg, Healy and Fuerstenau, 1966).

3.3.2.4 Potential Energy of Interaction between Two Spherical Particles

Derjaguin (1939) considers that provided the thickness of the double layers is small compared with the particle size, the interaction between double layers on spherical particles may be assumed to be made up of contributions from infinitesimally small parallel rings each of which can be considered as a flat plate (Figure 3.5).

The energy of interaction, V_R , between two spherical double layers is then given by

$$V_R = \int_0^\infty 2\pi h V_I dh \quad (3.63)$$

where V_I comes from expression (3.62) and h is the radius of the elementary ring as shown in Figure 3.5. From the geometry of the of the system

$$H - H_0 = a_1 + a_2 - \sqrt{a_1^2 - h^2} - \sqrt{a_2^2 - h^2} \quad (3.64)$$

Differentiation with respect to H yields

$$dh = \left(\frac{1}{a_1 \sqrt{1 - \frac{h^2}{a_1^2}}} + \frac{1}{a_2 \sqrt{1 - \frac{h^2}{a_2^2}}} \right) h dh \quad (3.65)$$

which, for $h \ll a_1$ and $h \ll a_2$, reduces to

$$h dh \approx \left(\frac{a_1 a_2}{a_1 + a_2} \right) dH \quad (3.66)$$

Therefore

$$V_R = \frac{2\pi a_1 a_2}{a_1 + a_2} \int_{H_0}^{\infty} V_I(H) dH \quad (3.67)$$

The quantity H is identical to the distance, $2d$, between the plates in equation (3.62) so that the above integral can be evaluated analytically giving

$$V_R = \frac{\epsilon a_1 a_2 (\psi_{01}^2 + \psi_{02}^2)}{4(a_1 + a_2)} \left[\frac{2\psi_{01}\psi_{02}}{(\psi_{01}^2 + \psi_{02}^2)} \ln \left(\frac{1 + \exp(-\kappa H_0)}{1 - \exp(-\kappa H_0)} \right) + \ln(1 - \exp(-2\kappa H_0)) \right] \quad (3.68)$$

This solution only holds exactly for values of ψ_{01} and ψ_{02} of less than 25 mV and for solution conditions such that the double layer thickness is small compared with the particle size.

Equation (3.68) is, however, shown to be a good approximation for systems in which ψ_{01} and ψ_{02} are less than 50 - 60 mV (Hogg et al, 1966). Verwey and Overbeek (1948) have shown that Derjaguin's method gives a good approximation for the interaction provided the product $\kappa a > 10$, and that the approximation is not too bad for $\kappa a > 5$.

For identical spherical particles, i.e. $\psi_{01} = \psi_{02} = \psi_0$, $a_1 = a_2 = a$, equation (3.68) reduces to

$$V_R = \frac{8a\psi_0^2}{2} \ln [1 + \exp(-\kappa H_0)] \quad (3.69)$$

3.3.2.5 The Repulsion Force between Two Spheres

To obtain the repulsion force for two unequal spheres of different surface charges, equation (3.68) can be derived with respect to H_0 . Therefore,

$$F_R = \frac{dV_R}{dH_0}$$

or

$$F_R = \frac{\epsilon a_1 a_2 (\psi_{01}^2 + \psi_{02}^2)}{4(a_1 + a_2)} \left[\frac{2\psi_{01}\psi_{02}}{(\psi_{01}^2 + \psi_{02}^2)} \left(\frac{-2\kappa \exp(-\kappa H_o)}{1 - \exp(-2\kappa H_o)} \right) + \frac{2\kappa \exp(-2\kappa H_o)}{1 - \exp(-2\kappa H_o)} \right] \quad (3.70)$$

3.3.3 The London/van der Waals Attraction

The existence of an attraction potential between the atoms and macroscopic bodies has been a well established fact in the field of colloid stability. These attractive or van der Waals forces consist of three components which all give rise to an attractive energy varying inversely as the sixth power of the distance between the two atoms.

The only well known attractive forces are the London forces. These forces postulated by London are known as dispersion forces, as they arise from the same electronic oscillations which are responsible for the dispersion of light. London forces are known to be short range forces, of the order of atomic dimensions. In the case of colloidal particles the additivity of dispersion forces, however, lend them a much longer range. The London force can be described as such that in a neutral atom the zero point energy of the electrons generates a rapidly fluctuating dipole moment. The frequency of the fluctuation is of the order of the frequency of electronic movements, i.e. of the order of 10^{15} or 10^{16} per second. The fluctuating dipole of one atom polarises a neighbouring one and consequently the two atoms attract each other.

The other two components to the van der Waals forces, the orientation and the induction effects, which arise when one of the molecules possesses a permanent dipole can be ignored in many systems. London (1930) in fact showed that the dispersion forces are the

dominant forces except for extremely polar molecules.

3.3.3.1 The London/van der Waals Attraction between Two Spherical Particles

Considering only the contribution of the dispersion forces, the London energy between two atoms at a distance, r , is

$$V_{\text{LONDON}} = - \frac{\lambda_{12}}{r^6} \quad (3.71)$$

where λ_{12} is the London constant.

The energy of interaction between two particles containing q_1 and q_2 atoms per cm^3 , as given by Hamaker (1937), is

$$V_A = - \int_{V_1} q_1 dv_1 \int_{V_2} dv_2 \frac{q_2 \lambda_{12}}{r^6} \quad (3.72)$$

where dv_1 , dv_2 , V_1 and V_2 are volume elements and total volumes of the two particles respectively, r denotes the distance between dv_1 and dv_2 . The integration steps for this problem are given in Appendix 8. The result of integration yields to the following expression

$$V_A = - \frac{A_{12}}{6} \left[\frac{2R_1 R_2}{C^2 - (R_1 + R_2)^2} + \frac{2R_1 R_2}{C^2 - (R_1 - R_2)^2} + \ln \frac{C^2 - (R_1 + R_2)^2}{C^2 - (R_1 - R_2)^2} \right] \quad (3.73)$$

$$\text{where } A_{12} = \pi^2 q_1 q_2 \lambda_{12} \quad (3.74)$$

$$C = R_1 + R_2 + S$$

This relation expresses the attraction energy, V_A , as a function of the radii R_1 and R_2 and of the distance between the centres, C .

For S much smaller than the particle size, V_A reduces to

$$V_A = - \frac{A_{12}}{6} \frac{R_1 R_2}{S(R_1 + R_2)} \quad (3.75)$$

The constant, A_{12} , which depends on the nature of two interacting materials, is known as the Hamaker constant.

When the two interacting bodies are separated by a third medium, Hamaker showed that the expression (3.73) could still be used provided that the Hamaker constant was modified according to

$$A = A_{12} + A_{33} - A_{13} - A_{23} \quad (3.76)$$

where Hamaker constants A_{ij} are for the materials i and j in vacuo.

This formulae was later shown to predict lower values than expected due to the neglect of interaction between medium 3 with the materials 1 and 2. For water as the medium 3, equation (3.76) should be multiplied by 1.5 to produce a better approximation (van den Tempell, 1972).

In order to calculate Hamaker constants for different materials, it is necessary to have a means of calculating the London constant, λ . This constant is determined by the nature of the interacting atoms and its value for any given material must be obtained from atomic properties.

The classical method for calculation of λ is based on the assumption of additivity of intermolecular dispersion forces. The theory originates from the expression for dispersion energy between hydrogen like atoms given by London.

The London constant for two different atoms is given as below,

$$\lambda_{12} = \frac{3h e^4}{32\pi^4 m_e^2} \sum_1 \sum_2 \frac{f_1 f_2}{\nu_1 \nu_2 (\nu_1 + \nu_2)} \quad (3.77)$$

where h is the Plank constant, e and m_e are the charge and mass of the electron, f_1 and f_2 are the oscillator strengths corresponding to transition frequencies of the electron ν_1 and ν_2 in atoms 1 and 2.

For those materials whose variation of refractive index with frequency can be represented by a dispersion equation with only one term, (Gregory, 1969) equation (3.77) can be reduced to the following expression,

$$\lambda_{12} = \frac{3he^4}{32 \pi^4 m_e^2} \frac{s_1 s_2}{v_{1v} v_{2v} (v_{1v} + v_{2v})} \quad (3.78)$$

and for the interaction between similar atoms

$$\lambda = \frac{3he^4}{64 \pi^4 m_e^2} \frac{s^2}{v_v^3}$$

where $s = \sum f$ and is regarded as the effective number of dispersion electrons, and v_v is a characteristic frequency.

To obtain the Hamaker constant, A , for the condensed media, λ_{12} can be replaced in equation (3.74). Where the bodies are immersed in a liquid, the Hamaker constant is obtained from (3.76), provided that dispersion data for the liquid are available.

Another approach to calculate the London constant is the macroscopic approach of Lifshitz. The principle is that the electromagnetic field originating from the rapidly rotating atomic dipoles in one particle interacts with the atomic dipoles in another particle. The fluctuating electromagnetic field and its interaction with any other condensed material can be measured directly by recording the amount of light reflected from the surface of the body over the entire range of frequencies from zero to infinity. The important quantity that determines interaction is the amount of electromagnetic energy absorbed at each frequency.

The Hamaker constant for a system comprising two semi infinite flat plates of dielectric constants ϵ_1 and ϵ_2 separated by a medium of dielectric constant ϵ_3 is-

$$A = \frac{3h}{8\pi^2} \int_0^\infty \left[\frac{\epsilon_1(i\xi) - \epsilon_3(i\xi)}{\epsilon_1(i\xi) + \epsilon_3(i\xi)} \right] \left[\frac{\epsilon_2(i\xi) - \epsilon_3(i\xi)}{\epsilon_2(i\xi) + \epsilon_3(i\xi)} \right] d\xi \quad (3.79)$$

where h is the Plank constant and $\epsilon_1, \epsilon_2, \epsilon_3$ are real function of the complex frequency, $\omega = \omega' + i\xi$, ($\omega = 2\pi\nu$) (Dzyaloshinskii et al, 1960).

As for many systems, the value of the Hamaker constant is not

available, it is possible to obtain an approximate value for A in terms of the known ones through combining rules, one of which has already been discussed, equation (3.76). Also, the simple geometric mean rule, equation (3.80), is shown to provide a good approximation (Israelachvili and Tabor, 1973).

$$A_{12} = \sqrt{A_{11} A_{22}} \quad (3.80)$$

Other expressions for combining rules are

$$A_{131} = (A_{11}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}})^2 \quad (3.81)$$

$$A_{131} = A_{11} + A_{33} - 2A_{13} \quad (3.82)$$

$$A_{132} = (A_{22}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}})(A_{11}^{\frac{1}{2}} - A_{33}^{\frac{1}{2}}) \quad (3.83)$$

The validity of these expressions has been examined by Owens and Richmond (1978) for water-oil-air system. They concluded that, except for equation (3.80), the results from the rest of the expressions were sometimes out by orders of magnitude, particularly in cases where small numbers were predicted by subtraction of two large numbers.

3.3.3.2 Retarded London/van der Waals Forces

Due to the electromagnetic nature of dispersion forces, they are subject to retardation. At large distances the forces are greatly reduced because the finite time required for their propagation causes a phase difference between the electronic oscillations of interacting molecules.

Casimir and Polder (1948) investigated the effect by means of quantum electrodynamics and found that at very large separations the intermolecular potential was considerably reduced, varying as the inverse seventh power of distance. Over the whole range of separations, the result may be expressed as a correction function to be applied to the

London energy.

$$V_A = - \frac{\lambda_{12}}{r^6} f(p)$$

where $p = \frac{2\pi r}{\lambda_c}$, and λ_c is the characteristic wavelength of the interaction.

There is no single expression for the function $f(p)$, but Overbeek (1952) gives two empirical correlations as follows

$$\begin{aligned} f(p) &= 1.01 - 0.14p & 0 < p < 3 \\ f(p) &= \frac{2.45}{p} - \frac{2.04}{p^2} & 0 < p < \infty \end{aligned} \quad (3.84)$$

The expression for $f(p)$ should be used in a Hamaker type integration to find the retarded force between two bodies. The integration faces difficulties when both of the functions are needed in the calculations. Therefore, fitting a single function to $f(p)$ should be desirable.

Schenkel and Kitchener (1960) have fitted the following expression for $f(p)$ which is accurate within 10% for the range $0.5 < p < \infty$.

$$f(p) \approx \frac{2.73}{(p+2.14)} \quad (3.85)$$

Use of this equation leads into difficulties in the integration procedure.

A suitable expression suggested by Schenkel and Kitchener is expression (3.86), which gives an error of 5% for the range $1 < p < \infty$ and is applicable down to $p = 0.5$ with maximum error

$$f(p) \approx \frac{2.45}{p} - \frac{2.17}{p^2} + \frac{0.59}{p^3} \quad (3.86)$$

of 15% occurring at $p = 0.64$ but must not be used for $p < 0.5$.

For $p < 0.5$, they proposed an empirical expression for the London/van der Waals potential of interaction for two equal spheres, which adequately represents the region $0 < p < 2$.

$$V_A \approx \frac{AR_1}{12S} \left(\frac{1}{1+1.77p} \right) \quad S \ll R_1 \quad (3.87)$$

where R_1 is the radius of the spheres and S is the minimum distance between them.

In the next section, the retarded energy of interaction will be calculated for two unequal spheres using expression (3.86) for $f(p)$. An expression of the type (3.87) is also used to predict the potential for $p < 0.5$.

3.3.3.3 Calculation of Retarded Forces for Two Spheres

To calculate the retarded force, relation (3.86) was used for $f(p)$. This relation is used in the expression for V_p (Appendix 8) to calculate the attraction potential between a point p and a sphere of radius R_1 .

$$V_p = \frac{-\pi q_1 \lambda_{12}}{R} \int_{R-R_1}^{R+R_1} \frac{1}{r^5} f(p) [R_1^2 - (R-r)^2] dr \quad (3.88)$$

or

$$I_p = \int_{R-R_1}^{R+R_1} \frac{1}{r^5} \left(G + 2Rr - r^2 \right) \left(\frac{A}{r} - \frac{B}{r^2} + \frac{Q}{r^3} \right)$$

where

$$G = R_1^2 - R^2$$

$$A = \frac{2.45}{2\pi} \lambda_c$$

$$B = \frac{2.17}{4\pi^2} \lambda_c^2$$

$$Q = \frac{0.59}{8\pi^3} \lambda_c^3$$

Carrying out the integration and applying the limits, I_p is obtained as

$$\begin{aligned}
 I_P = G & \left[-\frac{A}{5} \left(\frac{1}{(R+R_1)^5} - \frac{1}{(R-R_1)^5} \right) + \frac{B}{6} \left(\frac{1}{(R+R_1)^6} - \frac{1}{(R-R_1)^6} \right) \right. \\
 & \left. - \frac{Q}{7} \left(\frac{1}{(R+R_1)^7} - \frac{1}{(R-R_1)^7} \right) \right] + 2R \left[-\frac{A}{4} \left(\frac{1}{(R+R_1)^4} - \frac{1}{(R-R_1)^4} \right) \right. \\
 & + \frac{B}{5} \left(\frac{1}{(R+R_1)^5} - \frac{1}{(R-R_1)^5} \right) - \frac{Q}{6} \left(\frac{1}{(R+R_1)^6} - \frac{1}{(R-R_1)^6} \right) \left. - \left[-\frac{A}{3} \left(\frac{1}{(R+R_1)^3} \right. \right. \right. \\
 & \left. \left. - \frac{1}{(R-R_1)^3} \right) + \frac{B}{4} \left(\frac{1}{(R+R_1)^4} - \frac{1}{(R-R_1)^4} \right) - \frac{Q}{5} \left(\frac{1}{(R+R_1)^5} - \frac{1}{(R-R_1)^5} \right) \right] \quad (3.89)
 \end{aligned}$$

The integration for V_A can next be conducted as follows

$$V_A = -\frac{\lambda_{12} q_1 q_2 \pi^2}{C} \int_{C-R_2}^{C+R_2} I_P (D + 2C R - R^2) dR \quad (3.90)$$

or

$$I = \int_{C-R_2}^{C+R_2} I_P (D + 2C R - R^2) dR$$

where

$$D = R_2^2 - C^2$$

After some lengthy algebraic manipulations and applying the limits, the expression for V_A is obtained.

$$\begin{aligned}
 V_A = -\frac{\lambda_{12} q_1 q_2 \pi^2}{C} & \left[H_1 \ln \frac{X_1 Y_2}{Y_1 X_2} + S_1(X_1 - Y_1) + S_2(X_1^2 - Y_1^2) + S_3(X_1^3 - Y_1^3) \right. \\
 & + S_4(X_1^4 - Y_1^4) + S_5(X_1^5 - Y_1^5) + T_1(X_2 - Y_2) + T_2(X_2^2 - Y_2^2) \\
 & \left. + T_3(X_2^3 - Y_2^3) + T_4(X_2^4 - Y_2^4) + T_5(X_2^5 - Y_2^5) \right] \quad (3.91)
 \end{aligned}$$

where

$$X_1 = \frac{1}{C+R_2+R_1}$$

$$Y_1 = \frac{1}{C-R_2+R_1}$$

$$X_2 = \frac{1}{C+R_2-R_1}$$

$$Y_2 = \frac{1}{C-R_2-R_1}$$

H_1 , S 's and T 's are all constants and functions of the parameters in the expression for $f(p)$ and the geometry of the system. Their values are given separately in Appendix 9.

To obtain the expression for the dispersion forces between two spheres, equation (3.91) should be derived with respect to the surface separation distance, S .

$$F_A = \frac{\partial V_A}{\partial S} = \frac{\partial V_A}{\partial C} \quad (3.92)$$

As

$$V_A = -A \times \frac{1}{C} \times I$$

where

$$A = \lambda_{12} q_1 q_2 \pi^2$$

Therefore

$$\frac{\partial V_A}{\partial C} = -A \left[-\frac{I}{C^2} + \frac{\partial I}{\partial C} \times \frac{1}{C} \right]$$

When the derivation is carried out the expression for F_A is as follows

$$\begin{aligned} F_A = -A \left[(X_1 - Y_1) \left(-\frac{2H_1}{C} - \frac{S_1}{C^2} \right) + (X_2 - Y_2) \left(\frac{2H_1}{C} - \frac{T_1}{C^2} \right) \right. \\ + (X_1^2 - Y_1^2) \left(-\frac{S_1}{C} + \frac{S_{22}}{C} - \frac{S_2}{C^2} \right) + (X_2^2 - Y_2^2) \left(-\frac{T_1}{C} + \frac{T_{22}}{C} - \frac{T_2}{C^2} \right) \\ + (X_1^3 - Y_1^3) \left(-\frac{2S_2}{C} + \frac{S_{33}}{C} - \frac{S_3}{C^2} \right) + (X_2^3 - Y_2^3) \left(-\frac{2T_2}{C} + \frac{T_{33}}{C} - \frac{T_3}{C^2} \right) \\ + (X_1^4 - Y_1^4) \left(-\frac{3S_3}{C} + \frac{S_{44}}{C} - \frac{S_4}{C^2} \right) + (X_2^4 - Y_2^4) \left(-\frac{3T_3}{C} + \frac{T_{44}}{C} - \frac{T_4}{C^2} \right) \\ + (X_1^5 - Y_1^5) \left(-\frac{4S_4}{C} + \frac{S_{55}}{C} - \frac{S_5}{C^2} \right) + (X_2^5 - Y_2^5) \left(-\frac{4T_4}{C} + \frac{T_{55}}{C} - \frac{T_5}{C^2} \right) \\ \left. - \frac{5S_5}{C} (X_1^6 - Y_1^6) - \frac{5T_5}{C} (X_2^6 - Y_2^6) - 8H_1 R_1 R_2 X_1 Y_1 X_2 Y_2 - \frac{H_1}{C^2} \ln \frac{X_1 Y_2}{Y_1 X_2} \right] \end{aligned} \quad (3.93)$$

The constants in this equation are given in Appendix 9.

3.3.3.4 Calculation of the Correction Factor

The expression for non retarded attraction energy (equation (3.73)) can be written as follows

$$V_A = -\frac{A_{12}}{6} \left[\frac{2R}{x^2+2xR+2x} + \frac{2R}{x^2+2xR+4R+2x} + \ln \frac{x^2+2xR+2x}{x^2+2xR+2x+4R} \right] \quad (3.94)$$

where

$$x = \frac{S}{R_1}, \quad R = \frac{R_2}{R_1}$$

Deriving equation (3.94) with respect to minimum surface separation, S , leads to an expression for the attraction force. The procedure is as follows.

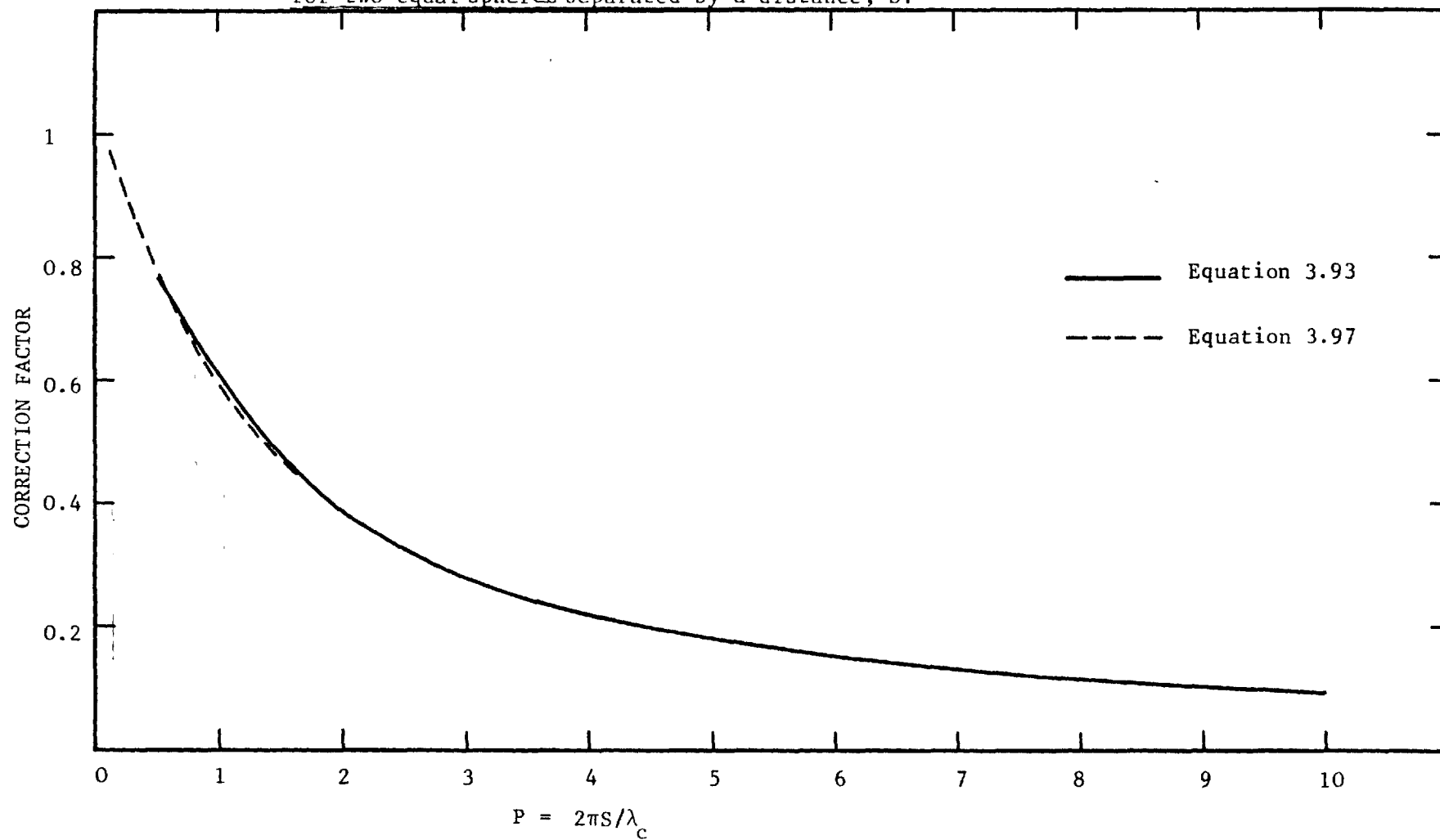
$$\begin{aligned} F &= \frac{\partial V_A}{\partial S} = \frac{\partial V_A}{\partial x} \times \frac{\partial x}{\partial S} \\ \frac{\partial x}{\partial S} &= \frac{1}{R_1} \\ F &= \frac{1}{R_1} \frac{\partial V_A}{\partial x} \\ F &= -\frac{2A}{3R_1} (x+R+1) \left[\frac{-R}{(x^2+2Rx+2x)^2} - \frac{R}{(x^2+2Rx+4R+2x)^2} \right. \\ &\quad \left. + \frac{2R}{(x^2+2Rx+2x)(x^2+2Rx+2x+4R)} \right] \end{aligned} \quad (3.95)$$

The correction factor, C_f , can then be calculated as follows

$$F_A = F \times C_f$$

As equation (3.93) for F_A is valid only over $0.5 < p < \infty$, the expression given by Schenkel and Kitchener (1960) is used to predict the retarded dispersion forces over the range $0 < p < 2$.

FIGURE 3.6: Correction factor for calculation of retarded London/van der Waals forces for two equal spheres separated by a distance, S .



$$V_A = - \frac{A}{6S} \frac{R_1 R_2}{(R_1 + R_2)} \frac{1}{(1 + 1.77p)} \quad (3.96)$$

$$F_A = - \frac{A}{6} \frac{R_1 R_2}{(R_1 + R_2)} \left[- \frac{1}{S^2} \frac{1}{(1 + 1.77p)} - \frac{1}{S} \frac{1.77 \frac{2\pi}{\lambda}}{(1 + 1.77p)^2} \right] \quad (3.97)$$

In the region where the two solutions overlap, an arithmetic mean of both the expressions (3.93) and (3.97) is used to predict the correction factor.

A subroutine (SUBROUTINE LONDON) was written in order to calculate the correction factor, C_f .

Figure 3.6 shows a plot of C_f versus $p \left(\frac{2\pi S}{\lambda_c} \right)$ for two equal spheres. This curve was checked against the results produced by Schenkel and Kitchener and good agreement was found.

3.3.4 The Total Potential Energy and Force of Interaction between Two Spheres

In order to obtain the total energy of interaction and force between two spheres, the expressions for energy and force due to interaction of double layers (3.68, 3.70) were combined with those for attraction (3.91, 3.93, 3.95, 3.96 and 3.97).

For any system consisting of two particles (spheres) suspended in a medium, calculation of the total energy of interaction and force is possible provided that the surface potential of the particles as well as the Hamaker constant for that particular system are known.

The surface potential which is often approximated by the ζ potential can be obtained through electromobility measurements.

To convert the electromobility data into ζ potential, a suitable correlation must be employed. For a particle of radius a , if κa is large, i.e. greater than 300, Smoluchowski's

equation (Shaw, 1969) applies. This equation reads

$$u_E = \frac{\zeta \epsilon}{4\pi\mu}$$

where u_E is the electromobility of the particle, and ϵ and μ are the dielectric constant and the viscosity of the medium, respectively.

When κa is small, i.e. smaller than 0.5, Hückel's equation holds accurately.

$$u_E = \frac{\zeta \epsilon}{6\pi\mu}$$

The Hückel equation is not likely to be applicable to particle electrophoresis in aqueous media. However, it does have possible applicability to electrophoresis in non-aqueous media of low conductance.

For κa between these two limits, the relation between u_E and ζ becomes a function of κa . The appropriate approach in this case to calculate ζ is given by Wiersema, Loeb and Overbeek (1966).

Typically, for an oil particle 3.2 μm in diameter in a solution $2 \times 10^{-3} \text{ M}\ell^{-1} \text{ Na}_2 \text{ SO}_4$, at 25°C, the value of κa is 409.

For calculation of repulsion forces in this work, the surface potential was always approximated by the value of ζ potential.

In order to obtain an estimation of Hamaker constant for the system decane-water-air, Lifshitz theory was employed in conjunction with the best available data on the permittivities of each component as a function of imaginary frequencies. The procedure for calculating the Hamaker constants for air-n-alkanes-water systems is given by del Cerro and Jameson (1979). A computer program kindly provided by the authors was run for the system mentioned above, and a value of $A_{132} = -0.247 \times 10^{-13}$ ergs was obtained.

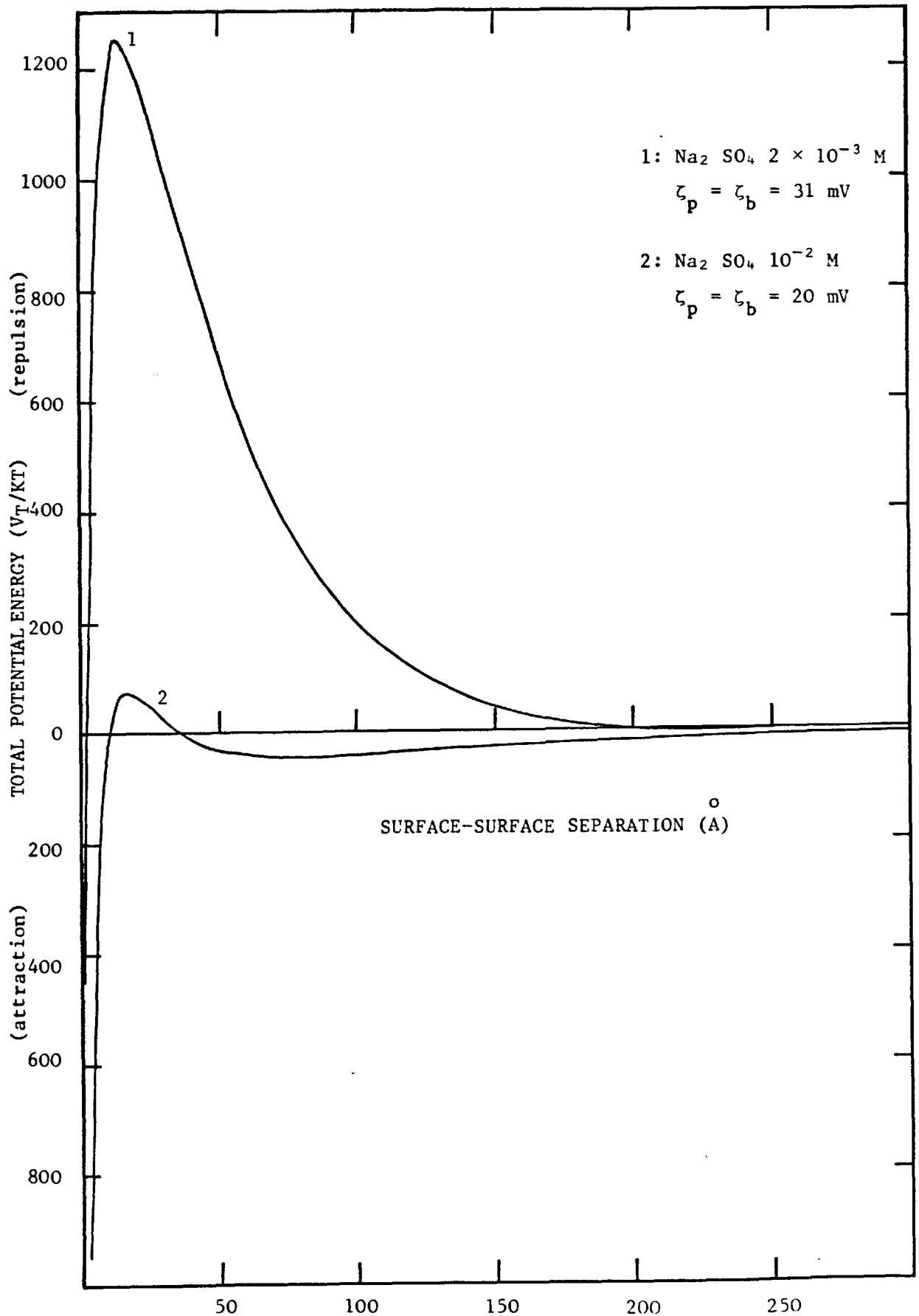
The negative sign suggests repulsion rather than attraction between the oil and air when separated by a film of water. In other words, the water film would be stable and it therefore could be concluded that the surfaces are hydrophilic.

As oil particles and air bubbles can certainly be considered to be hydrophobic, and, on the other hand, the fact that the particles have been captured by the bubbles experimentally, shows that an attractive force should act at a certain distance between them. Therefore, due to unavailability of a better model for attractive forces between condensed bodies in aqueous media, a value of 10^{-13} ergs was chosen as the effective Hamaker constant throughout the calculations.

A subroutine (SUBROUTINE MOLFORC) was written to calculate both intermolecular potential energy and force for two spheres approaching each other. Figure 3.7 shows a plot of potential energy of interaction between a bubble and a small oil particle for two different salt concentrations, as obtained by the computer program. A drastic fall in repulsion between the bubble and the oil particle can be clearly observed as the concentration of salt decreases from $2 \times 10^{-3}M$ to $10^{-2}M$.

FIGURE 3.7: The potential energy of interaction between an oil particle and a bubble

$$d_p = 3.2 \mu\text{m}, d_b = 330 \mu\text{m}, A_{132} = 10^{-13} \text{ ergs.}$$



3.4 Motion of a Sphere in a Viscous Fluid

The simple harmonic and rectilinear oscillations of a sphere in a viscous fluid were first investigated by Stokes (1851). By omitting the convective acceleration terms in the Navier-Stokes equations, he produced an expression consisting of two terms for the force exerted by the fluid on sphere, one involving the acceleration and the other the velocity. Both terms included viscosity.

Later Basset (1888), Boussinesq (1885) and Oseen (1927) studied the rectilinear motion of a sphere in a viscous fluid. They also omitted the convective acceleration terms in the Navier-Stokes equations in deriving their expression for force. They agreed that the force exerted by the fluid on a sphere depended not only on the instantaneous velocity and acceleration of the sphere but also on an integral term which represented the effect of its entire history of acceleration. Their expression, which is valid for a slowly moving but rapidly accelerating sphere in viscous flow, is

$$F = 6\pi\mu UR + \frac{1}{2}(\frac{4}{3}\pi R^3\rho_f) \frac{dU}{dt} + 6\pi\rho_f R^2 \sqrt{\frac{\mu}{\rho_f\pi}} \int_0^t \frac{dU}{d\tau} \frac{d\tau}{\sqrt{(t-\tau)}} \quad (3.98)$$

where μ and ρ_f are the viscosity and the density of the fluid, respectively, and U and R are the velocity and radius of the sphere, and t is time.

As can be seen, each effect is represented by a separate term in this expression.

The first term on the right is equal to the steady state viscous drag on a sphere. The second term is the acceleration term or added mass which has got the same magnitude for an accelerating sphere in an inviscid fluid and does not include viscosity. The third term represents the effect of history of acceleration.

The motion of a sphere in a fluid can be described by the following

expression:

$$M \frac{dU}{dt} = F_{\text{gravity}} - F_{\text{buoyancy}} - F_{\text{drag}} \quad (3.99)$$

Replacing from equation (3.98) for F_{drag} , the final expression is:

$$\begin{aligned} \frac{4}{3} \pi R^3 \rho_s \frac{dU}{dt} = & \frac{4}{3} \pi R^3 g(\rho_s - \rho_f) - 6\pi\mu UR - \frac{1}{2} \left(\frac{4}{3} \pi R^3 \rho_f \right) \frac{dU}{dt} \\ & - 6\pi \rho_f R^2 \sqrt{\frac{\mu}{\pi \rho_f}} \int_0^t \frac{dU}{d\tau} \frac{d\tau}{\sqrt{(t-\tau)}} \end{aligned} \quad (3.100)$$

To allow for the proximity of another sphere, the terms in the equation (3.100) should be corrected. For the steady state drag term (Stokes drag term), this has already been discussed in detail in Section 3.2 of this chapter, where a correction factor, λ , is included in this term to allow for the presence of the other sphere.

$$F = 6\pi\mu UR\lambda$$

The effect of a second sphere on the added mass term is studied in Section 3.4.1, using a solution for potential flow for a two sphere system given by Jeffery (1912).

The contribution of the history of acceleration term to the equations of motion of two spheres is also discussed in Section 3.5.

3.4.1 The Virtual Mass

When a solid body moves through an incompressible fluid, it produces a drift in the fluid, such that the final positions of the particles are further on than those from which they started. The drift volume enclosed between the initial and final positions is equal to the volume corresponding to hydrodynamic mass (Darwin, 1953). In fact, the mass of the moving object

increases from M to a value of $M + KM'$ which is called the virtual mass, where the coefficient K depends on the shape of the body and the nature of the motion, and M' is the mass of the liquid displaced by the object.

The kinetic energy of an object moving with a velocity U in a medium is

$$T = \frac{1}{2} (M + KM') U^2 \quad (3.101)$$

Therefore, to calculate the value of hydrodynamic mass (added mass), the kinetic energy of the total system (liquid + solid) should be obtained.

The expression for the kinetic energy of liquid when the motion is irrotational, as given by Milne-Thomson (1955), is

$$T = -\frac{1}{2} \rho_f \int \phi \frac{\partial \phi}{\partial n} dS \quad (3.102)$$

where dn is an element of normal drawn into the liquid at the element dS of area of the bounding surface, and ρ_f is the fluid density.

Also,

$$dS = 2\pi \rho ds \quad \text{and} \quad -\frac{\partial \phi}{\partial n} = \frac{1}{\rho} \frac{\partial \psi}{\partial s}$$

where ds is an element of arc of the meridian curve of the boundary.

The kinetic energy can then be written as

$$T = \pi \rho_f \int \phi d\psi \quad (3.103)$$

After integrating by parts,

$$T = -\pi \rho_f \int \psi d\phi \quad (3.104)$$

Also,

$$\frac{\partial \phi}{\partial s} = \frac{1}{\rho} \frac{\partial \psi}{\partial n}$$

Therefore, the kinetic energy in terms of stream potential is

$$T = - \pi \rho_f \int \frac{\psi}{\rho} \frac{\partial \psi}{\partial n} ds \quad (3.105)$$

3.4.1.1 Calculation of Kinetic Energy

The differential equation defining irrotational flow is

$$\nabla^2 \phi = 0 \quad (3.106)$$

where

$$\nabla^2 = \frac{\partial^2}{\partial z^2} + \rho \frac{\partial}{\partial \rho} \left(\frac{\partial}{\rho \partial \rho} \right)$$

and ψ , ϕ are related through these relations

$$\frac{\partial \psi}{\partial \rho} = \rho \frac{\partial \phi}{\partial z} ; \quad \frac{\partial \psi}{\partial z} = - \rho \frac{\partial \phi}{\partial \rho}$$

The solution of (3.106) for the case of axisymmetrical flow has been given by Jeffery (1912) as

$$\psi = \frac{1}{\sqrt{\cosh \xi - \mu}} \sum_{n=0}^{\infty} \left[a_n \cosh(n+\frac{1}{2}) \xi + b_n \sinh(n+\frac{1}{2}) \xi \right] \times \\ (P_{n-1}(\mu) - P_{n+1}(\mu)) \quad (3.107)$$

where $\mu = \cos \eta$.

In order to calculate the kinetic energy, a_n and b_n should be calculated. For that, the condition of impenetrability on the surface of the two spheres can be applied.

$$U_{\xi} = - v(\underline{i}_z \cdot \underline{i}_{\xi}) \quad (3.108)$$

where in bi-spherical co-ordinates

$$U_{\xi} = \frac{c}{\rho} \frac{\partial \psi}{\partial \eta} ; \quad \underline{i}_z \cdot \underline{i}_{\xi} = - c \frac{\partial \rho}{\partial \eta}$$

c is the constant in the bi-polar co-ordinate system. Therefore

$$\frac{\partial}{\partial \eta} (\psi - \frac{1}{2} v \rho^2) = 0 \quad (3.109)$$

or

$$\psi - \frac{1}{2} \rho^2 v = 0 \quad (3.110)$$

Replacing ρ in the bi-polar co-ordinates and ψ from the relation (3.107), the following relation is obtained

$$\begin{aligned} \sum_{n=0}^{\infty} \left[a_n \cosh(n+\frac{1}{2})\xi + b_n \sinh(n+\frac{1}{2})\xi \right] (P_{n-1} - P_{n+1}) \\ = \frac{1}{2} \frac{c^2 \sin^2 \eta v}{(\cosh \xi - \cos \eta)^{3/2}} \end{aligned} \quad (3.111)$$

This equation after expanding the right hand side and expressing it in terms of Legendre polynomials can be written as

$$\begin{aligned} \left[a_n \cosh(n+\frac{1}{2})\xi + b_n \sinh(n+\frac{1}{2})\xi \right] \\ = \frac{1}{\sqrt{2}} c^2 v \frac{1}{\sinh|\xi|} \frac{n(n+1)}{(2n+1)} \left[e^{-(n-\frac{1}{2})|\xi|} - e^{-(n+\frac{3}{2})|\xi|} \right] \end{aligned} \quad (3.112)$$

The mathematical procedure leading to this result is given in Appendix 10.

Applying $\xi = \alpha$, $v = v_1$ and $\xi = \beta$, $v = v_2$ to (3.112), two equations are obtained which can be solved to find a_n and b_n .

To calculate the kinetic energy, equation (3.105) can be expressed in bipolar coordinates using the following relations

$$ds = \frac{-cd\eta}{(\cosh \xi - \mu)}$$

$$\frac{\partial}{\partial n} = -\frac{1}{c} (\cosh \xi - \mu) \frac{\partial}{\partial \xi}$$

$$\rho = \frac{c \sin \eta}{(\cosh \xi - \mu)}$$

where $\mu = \cos \eta$ and c is the constant in bi-polar co-ordinates.

Therefore

$$T = \pi \rho_f \int \frac{(\cosh \xi - \mu)}{c \sin \eta} \psi_P \frac{\partial \psi_P}{\partial \xi} d\eta \quad (3.113)$$

In order to evaluate T from the equation (3.113), $\frac{\partial \psi}{\partial \xi}$ should also be obtained. This is achieved by differentiating (3.107) with respect to ξ . The result as also obtained by Jeffery (1912) using the recurrence formula (3.114), is given below.

$$\mu [P_{n-1}(\mu) - P_{n+1}(\mu)] = \frac{n-1}{2n-1} [P_{n-2}(\mu) - P_n(\mu)] + \frac{n+2}{2n+3} [P_n(\mu) - P_{n+2}(\mu)] \quad (3.114)$$

$$\begin{aligned} \frac{\partial \psi}{\partial \xi} = & \frac{1}{2(\cosh \xi - \mu)^{\frac{1}{2}}} \sum_{n=0}^{\infty} \frac{n(n+1)}{2n+1} \left[\frac{1}{n+1} [(2n+1)a_n - (2n+3)a_{n+1}] \times \sinh(n+\frac{3}{2})\xi \right. \\ & - \frac{1}{n} [(2n-1)a_{n-1} - (2n+1)a_n] \sinh(n-\frac{1}{2})\xi \\ & + \frac{1}{n+1} [(2n+1)b_n - (2n+3)b_{n+1}] \cosh(n+\frac{3}{2})\xi \\ & \left. - \frac{1}{n} [(2n-1)b_{n-1} - (2n+1)b_n] \cosh(n-\frac{1}{2})\xi \right] V_n \quad (3.115) \end{aligned}$$

where

$$V_n = P_{n-1}(\mu) - P_{n+1}(\mu)$$

To obtain the kinetic energy from (3.115), a numerical technique was employed. The integration was performed using a fourth order Runge-Kutta method. For that, a library subroutine was used with variable integration step length to satisfy error requirements. Subroutine VIRTUAL was then written to calculate the kinetic energy for each sphere. To check the behaviour of the program, the kinetic energy obtained for a system of two equal spheres were

compared with the results obtained from the approximate solution to the problem given by Milne-Thomson (1955).

$$T = \frac{1}{4} M_1' U^2 + \frac{2\pi a^3 b^3 \rho_f}{C^3} UV + \frac{1}{4} M_2' V^2 \quad (3.116)$$

where M_1' , M_2' are the masses of liquid displaced by the respective spheres, a and b are the radii of the two spheres, U and V are their velocity of approach along the line of centres and C is the distance between the centres.

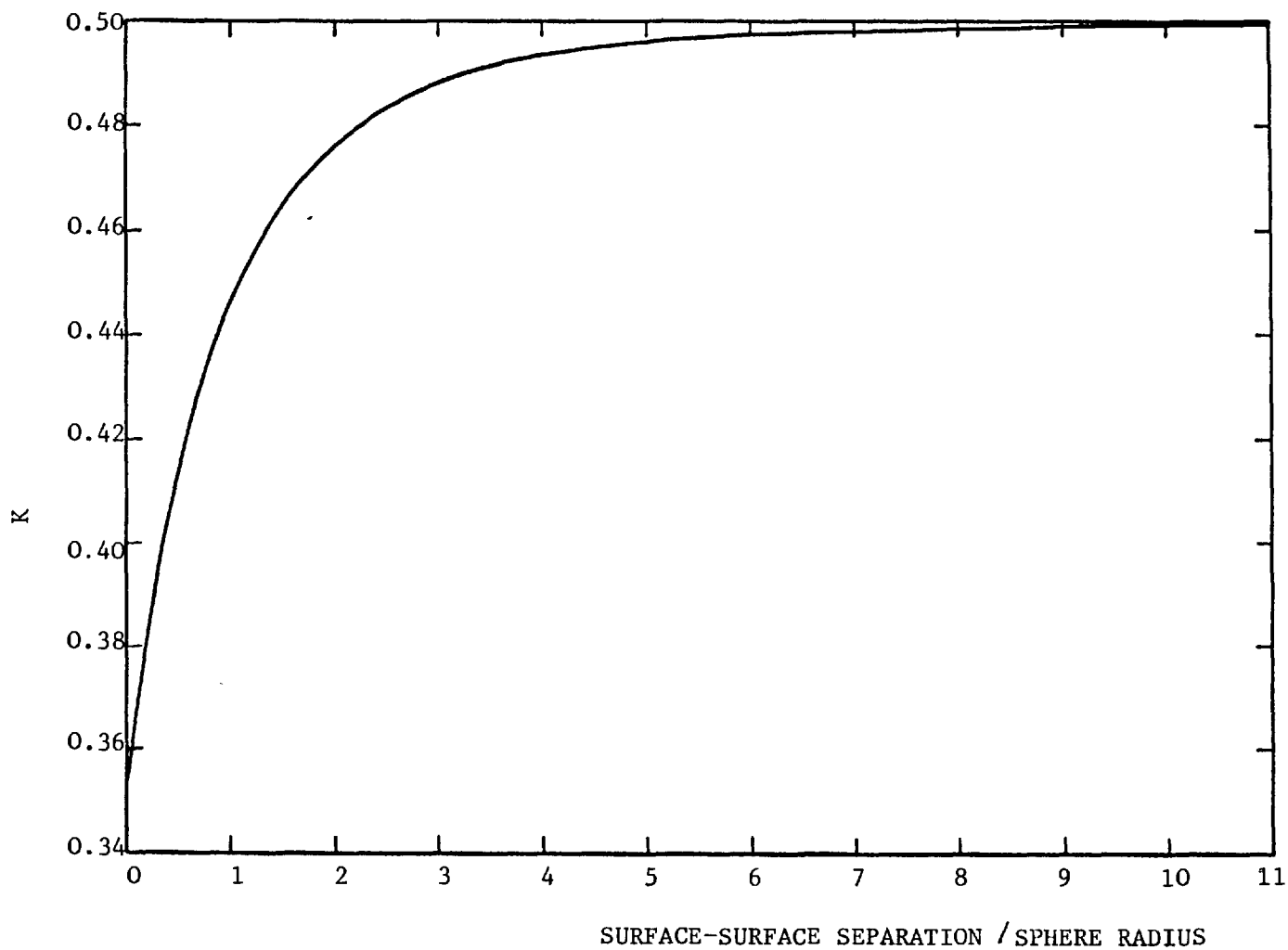
TABLE 3.9: Values for kinetic energy for two equal spheres moving along their line of centres

Centres distance/ a	$T_{\text{Milne-Thomson}}$	$T_{\text{This work}}$
12	2.0907	2.0907
10	2.0881	2.0881
8	2.0821	2.0821
6	2.0653	2.0654
5	2.0441	2.0445
4	1.9962	1.9980
3	1.8616	1.8733
2.5	1.6922	1.7310
2.25	1.5427	1.6207
2.1	1.4159	1.5382

The results of approximate solution start deviating from those obtained by the exact one when the spheres are less than one radius apart.

The coefficient, K , can be evaluated from the following

FIGURE 3.8: Values of K in the expression of virtual mass versus distance of separation between two equal spheres



equation

$$\frac{1}{2}(KM')U^2 = T$$

Therefore, to find K for each sphere under the influence of the other, it is enough to calculate T as mentioned.

Figure 3.8 shows a plot of K versus the dimensionless surface distance in a system of two equal spheres. As this graph shows, at a distance of about one radius, the value of K has decreased by almost 10% of that of single isolated sphere ($K = 0.5$), and when the two spheres are almost touching it has decreased by 30%.

3.5 Solution of the Equations of Motion of Two Spheres

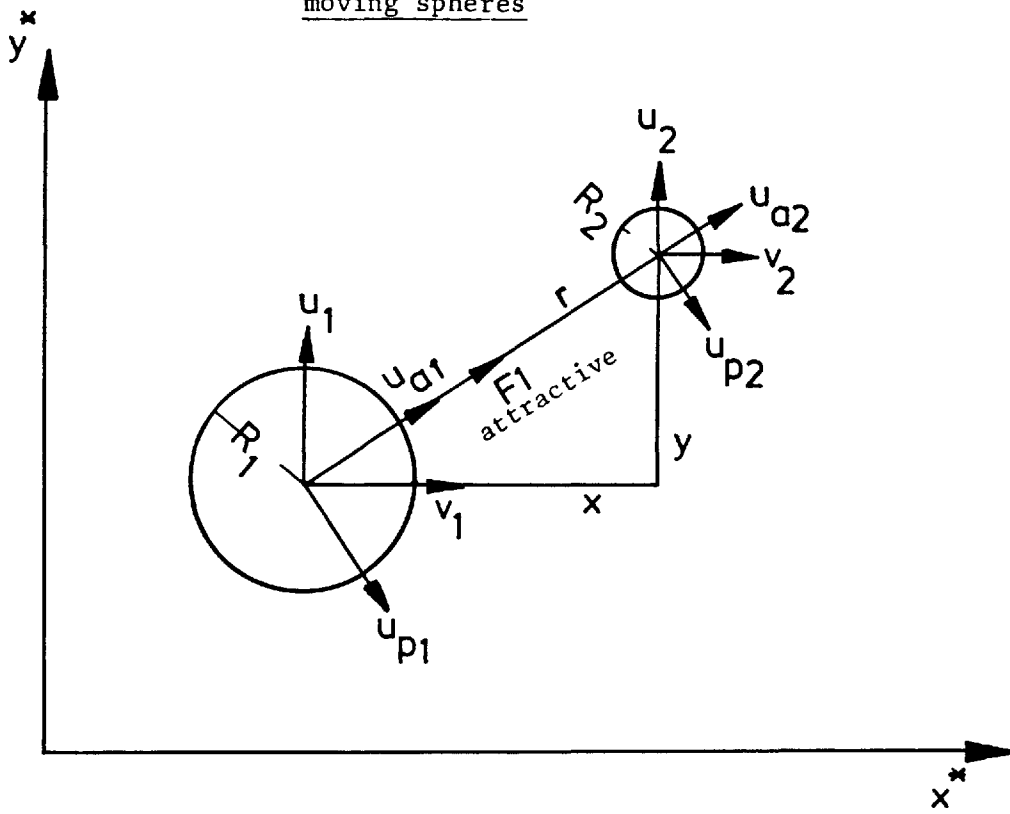
Consider a system of two spheres of radii R_1 and R_2 moving at arbitrary velocities with components both along the $\hat{x}$ and $\hat{y}$ axis as shown in Figure 3.9. The reference coordinate system is chosen such that gravity acts in the negative $\hat{x}$ direction.

As the equations of motion are linear, a complete calculation of the trajectories of both spheres can be obtained by superimposing the solutions for motions along and perpendicular to their line of centres obtained in previous sections.

Apart from hydrodynamic forces, attractive and repulsive forces of intermolecular origin are also included in the calculation.

The equations of motion for the spheres in terms of relative separations, x and y , can be written as follows:
in the x direction

FIGURE 3.9: The geometry of two arbitrarily moving spheres



for sphere R_1

$$\begin{aligned} \frac{4}{3} \pi R_1^3 \rho_1 \frac{dv_1}{dt} &= \frac{4}{3} \pi R_1^3 g(\rho_f - \rho_1) - 6\pi\mu R_1 (u_{a1} \lambda_{a1} \frac{x}{r} + u_{p1} \lambda_{p1} \frac{y}{r}) \\ &- 6\mu R_1^2 \sqrt{\frac{\pi}{v}} \int_0^t \frac{dv_1}{d\tau} \frac{d\tau}{\sqrt{t-\tau}} - \frac{4}{3} \pi R_1^3 \rho_f K \frac{dv_1}{dt} + F_{mol} \frac{x}{r} \end{aligned}$$

for sphere R_2 (3.117)

$$\begin{aligned} \frac{4}{3} \pi R_2^3 \rho_2 \frac{dv_2}{dt} &= \frac{4}{3} \pi R_2^3 g(\rho_f - \rho_2) - 6\pi\mu R_2 (u_{a2} \lambda_{a2} \frac{x}{r} + u_{p2} \lambda_{p2} \frac{y}{r}) \\ &- 6\mu R_2^2 \sqrt{\frac{\pi}{v}} \int_0^t \frac{dv_2}{d\tau} \frac{d\tau}{\sqrt{t-\tau}} - \frac{4}{3} \pi R_2^3 \rho_f K \frac{dv_2}{dt} - F_{mol} \frac{x}{r} \end{aligned}$$

(3.118)

in the y direction

for sphere R_1

$$\begin{aligned} \frac{4}{3} \pi R_1^3 \rho_1 \frac{du_1}{dt} &= - 6\pi\mu R_1 (u_{a1} \lambda_{a1} \frac{y}{r} - u_{p1} \lambda_{p1} \frac{x}{r}) \\ &- 6\mu R_1^2 \sqrt{\frac{\pi}{v}} \int_0^t \frac{du_1}{d\tau} \frac{d\tau}{\sqrt{t-\tau}} - \frac{4}{3} \pi R_1^3 \rho_f K \frac{du_1}{dt} + F_{mol} \frac{y}{r} \end{aligned}$$

for sphere R_2 (3.119)

$$\begin{aligned} \frac{4}{3} \pi R_2^3 \rho_2 \frac{du_2}{dt} &= - 6\pi\mu R_2 (u_{a2} \lambda_{a2} \frac{y}{r} - u_{p2} \lambda_{p2} \frac{x}{r}) \\ &- 6\mu R_2^2 \sqrt{\frac{\pi}{v}} \int_0^t \frac{du_2}{d\tau} \frac{d\tau}{\sqrt{t-\tau}} - \frac{4}{3} \pi R_2^3 \rho_f K \frac{du_2}{dt} - F_{mol} \frac{y}{r} \end{aligned}$$

(3.120)

where ρ_1 , ρ_2 and ρ_f are densities of spheres and fluid, respectively and F_{mol} is the sum of repulsive and attractive forces applied along the line of centres.

u_{a1} , u_{a2} , u_{p1} and u_{p2} can be written in terms of u_1 , u_2 , v_1 and v_2 as follows

$$u_{a1} = \frac{(v_1x + u_1y)}{r}$$

$$u_{a2} = \frac{(v_2x + u_2y)}{r}$$

$$u_{p1} = \frac{(v_1y - u_1x)}{r}$$

$$u_{p2} = \frac{(v_2y - u_2x)}{r}$$

λ_{a1} , λ_{p1} and λ_{a2} , λ_{p2} are the correction factors to the Stokes' drag term along and perpendicular to the line of centres for each of the spheres, R_1 and R_2 .

Two more equations can be written relating the relative change in the positions of the spheres to their velocities.

$$\frac{dx}{dt} = v_2 - v_1 \quad (3.121)$$

$$\frac{dy}{dt} = u_2 - u_1 \quad (3.122)$$

We thus have a system of six simultaneous first order differential equations for the velocities and relative positions of the particles which must be evaluated numerically.

The main problem that arises on attempting integration of the four equations (3.117 to 3.120) is that of evaluating the history of acceleration of each particle, i.e. the "history integral". A method on the lines of that employed by Clift (1975) was used to express this integral in terms of present and past values of the acceleration. The procedure is fully described in Appendix 11.

It is probably more convenient to handle the above equations in dimensionless form. Therefore, if the terminal velocity of sphere 1 and its corresponding radius are taken as the characteristic

velocity and length respectively, where the terminal velocity is given by

$$U_b = \frac{2}{9} \frac{(\rho_f - \rho_1) g R_1^2}{\mu}$$

the following dimensionless quantities can be defined

$$V_1 = \frac{v_1}{U_b}$$

$$V_2 = \frac{v_2}{U_b}$$

$$U_1 = \frac{u_1}{U_b}$$

$$U_2 = \frac{u_2}{U_b}$$

$$T = \frac{U_b t}{R_1}$$

$$X = \frac{x}{R_1}$$

$$Y = \frac{y}{R_1}$$

$$R = \frac{r}{R_1}$$

$$RA = \frac{R_2}{R_1}$$

Dividing both sides of equations (3.117 - 3.120) by either $6\pi\mu R_1$ or $6\pi\mu R_2$ and applying the definitions given above, the following equations are obtained.

$$\frac{dV_1}{dT} = \left[1 - (U_{a1} \lambda_{a1} \frac{X}{R} + U_{p1} \lambda_{p1} \frac{Y}{R}) - G_1 S_1 + \frac{F_{mol}}{F_b} \frac{X}{R} \right] \frac{1}{(E_1 + B_1 G_1)} \quad (3.123)$$

$$\frac{dV_2}{dT} = \left[H_2 - (U_{a2} \lambda_{a2} \frac{X}{R} + U_{p2} \lambda_{p2} \frac{Y}{R}) - G_2 S_2 - \frac{F_{mol}}{F_{pb}} \frac{X}{R} \right] \frac{1}{(E_2 + B_2 G_2)} \quad (3.124)$$

$$\frac{dU_1}{dT} = \left[(U_{p1} \lambda_{p1} \frac{X}{R} - U_{a1} \lambda_{a1} \frac{Y}{R}) - G_1 S_3 + \frac{F_{mol}}{F_b} \frac{Y}{R} \right] \frac{1}{(E_1 + B_3 G_1)} \quad (3.125)$$

$$\frac{dU_2}{dT} = \left[(U_{p2} \lambda_{p2} \frac{X}{R} - U_{a2} \lambda_{a2} \frac{Y}{R}) - G_2 S_4 - \frac{F_{mol}}{F_{pb}} \frac{Y}{R} \right] \frac{1}{(E_2 + B_4 G_2)} \quad (3.126)$$

$$\frac{dX}{dT} = V_2 - V_1 \quad (3.127)$$

$$\frac{dY}{dT} = U_2 - U_1 \quad (3.128)$$

Where the dimensionless groups in these expressions are

$$H_1 = \frac{2}{9} \frac{R_1^2}{\mu U_b} (\rho_f - \rho_1) g = 1$$

$$H_2 = RA^2 \left(\frac{\rho_f - \rho_2}{\rho_f - \rho_1} \right)$$

$$E_1 = \frac{2}{9} \frac{R_1 U_b \rho_1}{\mu} \left(1 + K \frac{\rho_f}{\rho_1} \right)$$

$$E_2 = \frac{2}{9} \frac{R_2^2 U_b \rho_2}{R_1 \mu} \left(1 + K \frac{\rho_f}{\rho_2} \right)$$

$$G_1 = \sqrt{\frac{R_1 U_b}{\pi \nu}}$$

$$G_2 = R_2 \sqrt{\frac{U_b}{R_1 \pi \nu}}$$

also

$$F_b = 6\pi\mu R_1 U_1$$

$$F_{pb} = F_b RA$$

and B's and S's are the contributions from history integral.

3.5.1 Grazing Trajectory

To calculate the trajectories described by both spheres, the set of simultaneous differential equations must be solved subject to initial conditions imposed on each of the dependent variables.

Integration was started for an initial horizontal separation, X_∞ , of 50, while the initial Y , Y_∞ , was varied until the critical one was found, that is, that for which one of the spheres just grazed the other. This critical value of Y was subsequently used to calculate collision efficiency.

As regards the rest of the dependent variables, initial values for a relative separation $(50, Y_\infty)$ were set as calculated from the approximate solution of Hestroni and Haber (1978) to avoid excessive computation time and error accumulation in the integration procedure. To check whether the initial distance of separation was large enough, a trajectory was calculated for $X_\infty = 100$ and no significant change in the collection efficiency was observed. Therefore, for all subsequent integrations a value of $X_\infty = 50$ was used.

Thus, the force required to maintain the motion of two spheres either in a direction along or perpendicular to their lines of centres as given by Hestroni and Haber (1978) read,
for sphere a :

$$\frac{F_{aA}}{6\pi\mu a} = K_{aA} U_{aA} + K_{bA} U_{bA} \quad (3.129-1)$$

$$\frac{F_{ap}}{6\pi\mu a} = K_{ap} U_{ap} + K_{bp} U_{bp} \quad (3.129-2)$$

for sphere b,

$$\frac{F_{bA}}{6\pi\mu b} = L_{bA} U_{bA} + L_{aA} U_{aA} \quad (3.129-3)$$

$$\frac{F_{bp}}{6\pi\mu b} = L_{bp} U_{bp} + L_{ap} U_{ap} \quad (3.129-4)$$

where F_A , U_A , F_p , U_p are the force and velocity components in the directions along and perpendicular to the line of centres, respectively.

K 's and L 's are functions of the geometrical configuration of the system, namely of the ratio of particle radius to centre to centre distance.

For two rigid spheres moving in an unbounded gravitational velocity field, a balance of forces on each sphere enables calculation of their velocities since

$$\frac{F_{iA}}{6\pi\mu r_i} = \frac{2}{9} \frac{\Delta\rho_i r_i^2}{\mu} g_A \quad (3.130-1)$$

and

$$\frac{F_{ip}}{6\pi\mu r_i} = \frac{2}{9} \frac{\Delta\rho_i r_i^2}{\mu} g_p \quad (3.130-2)$$

where the index i refers to sphere a or b . Also g_A and g_p are the components of gravitational acceleration either in a direction along or perpendicular to the line of centres. Therefore, substituting for $\frac{F_{iA}}{6\pi\mu r_i}$ and $\frac{F_{ip}}{6\pi\mu r_i}$ from (3.130) into (3.129), the velocity of each sphere can be obtained.

Different integration techniques were examined for the problem. First, a fourth order Runge-Kutta method with a variable integration step length was employed. The convergence of the method

was slow and the step length had to be drastically reduced in order to satisfy the error as the spheres came close to each other. Due to the long computing times needed, the method looked impractical to use.

The second method tried was a modified Euler method. This method was quite fast and accurate, but in some cases it became unstable again when the particles were very close.

The best and most stable of the methods was found to be Hamming's method. As with any other multistep integration procedure, it is necessary to use a single step method for the first steps before Hamming's method can be applied.

Here a modified Euler method was used to predict the initial points.

The integration subroutine employed automatically varied the step length to meet a prescribed error, and, whenever a halving or doubling of the step was required, the modified Euler method was used to predict the intermediate points.

To calculate the correction factors to the drag force, the approximate solution of Hestroni and Haber was used down to four bubble radius of centres separation, since it was found that this solution was in excellent agreement with the exact one up to separations of about one bubble diameter. Also, within this range, the modified Euler method was employed, as the method showed the same accuracy as Hamming's method and was comparatively faster.

For distances of separations below four bubble radii, the exact solution was used to predict the correction factors and Hamming's method was employed for integration.

Intermolecular forces were taken into account for distances

of separation below half a bubble radius since, for higher values, their effect was found to be practically negligible.

Referring to Figure 3.8, Section 3.4.1, it can be observed that the "added mass" term for two spheres system starts deviating from that for a single isolated sphere only at closed distances of approximation between spheres.

Considering that within the creeping flow approximations $Re < 0.5$, the contribution of the inertial term in the equations of motion is very small compared with the gravity and Stokes drag term, even at very close distances between spheres, it was therefore decided to take K as that corresponding to the single isolated sphere, i.e. 0.5, in order to avoid excessive computational time. The contribution of different terms in the equations of motion was actually observed by following their values as numerical integration proceeded.

To see the effect of the history of acceleration term, a trajectory was determined for the limiting condition of creeping flow approximation both with and without including the history integral. The trajectory of a 20 μm particle approaching a 100 μm bubble was found to be almost unaffected by this term. Therefore, the history integral was cancelled from the later calculations of efficiency.

A flow diagram representing the procedure for calculation of trajectory is given in Figure 3.10.

Figure 3.11 shows the grazing trajectory of a particle 50 μm in diameter and of a density of 2.5 gr cm^{-3} as it approaches a bubble of 200 μm in diameter in water. Attraction forces have been included assuming a Hamaker constant of $A_{132} = 10^{-13} \text{ ergs}$. No repulsion has been considered.

FIGURE 3.10: Flow diagram for trajectory calculation

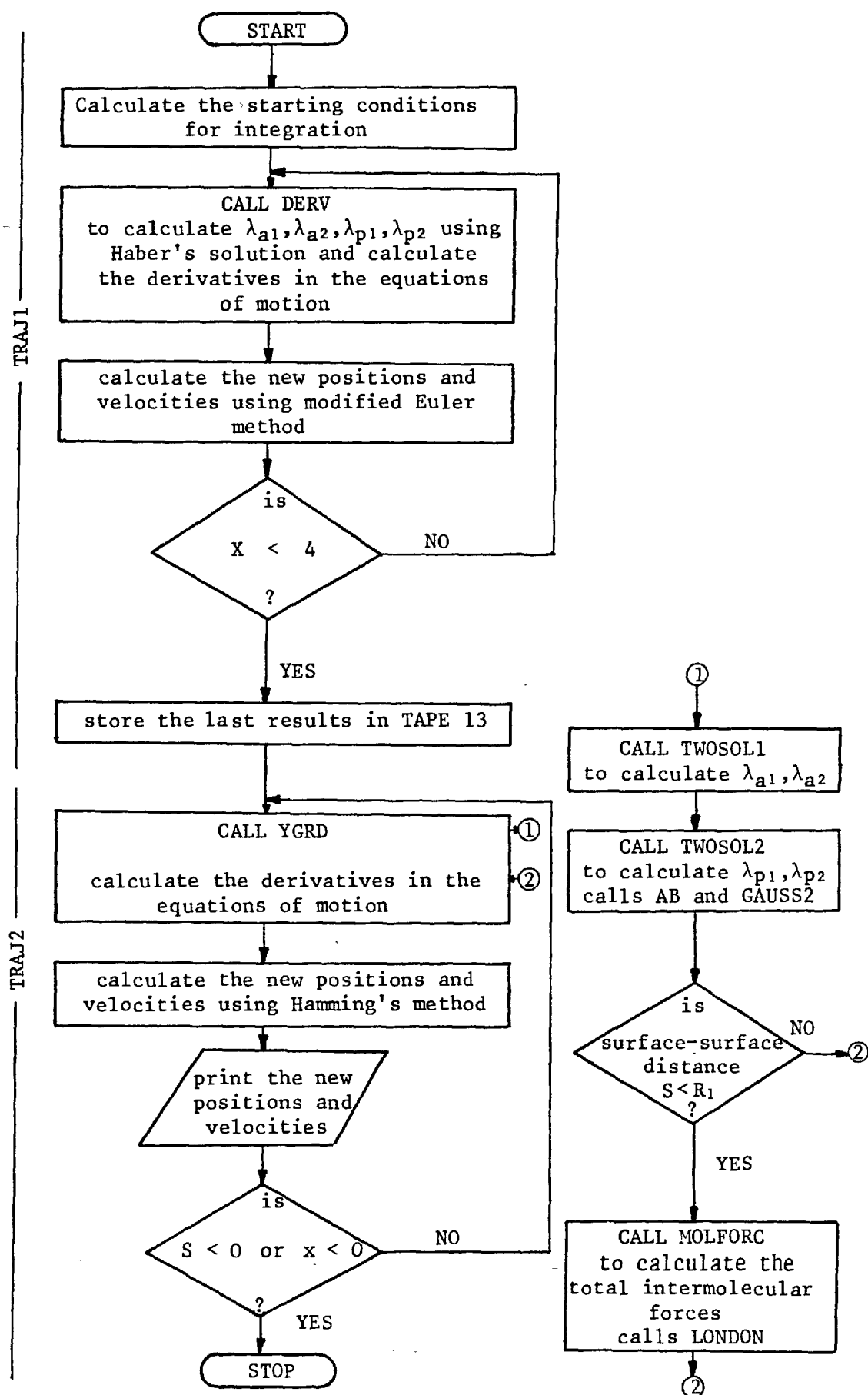
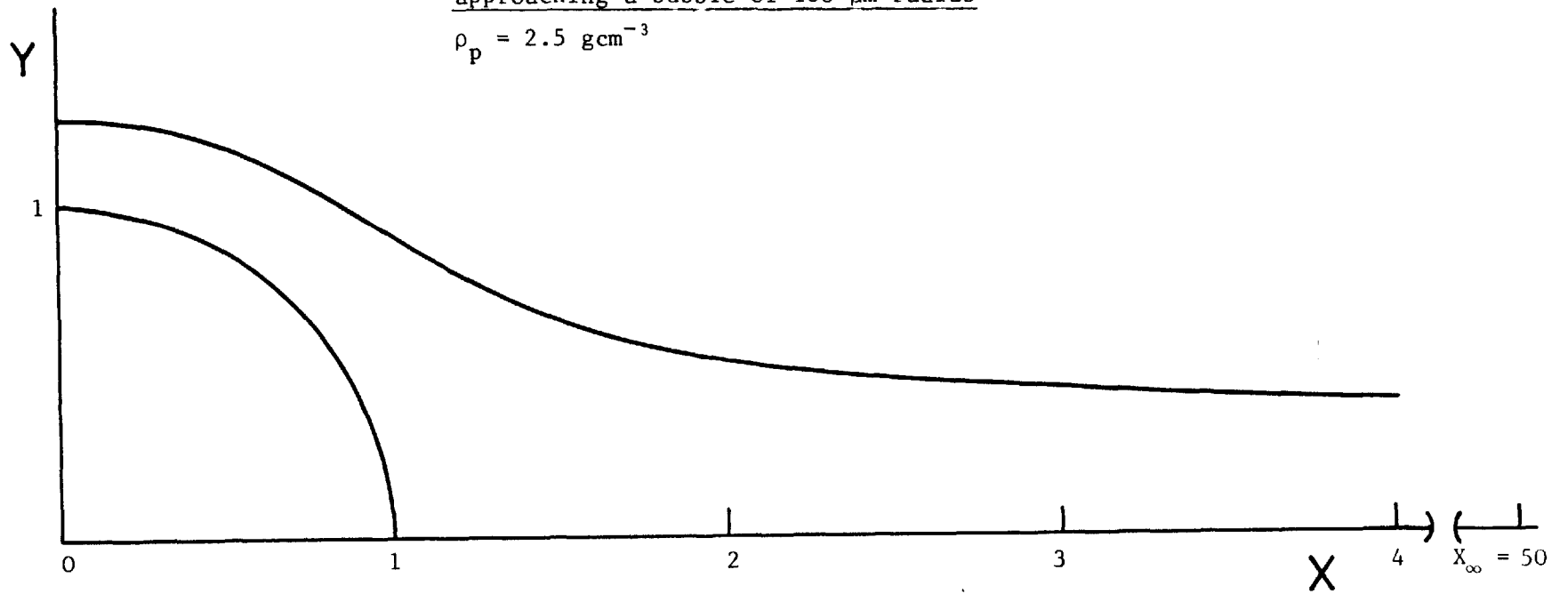


FIGURE 3.11: Grazing trajectory of a particle 25.8 μm in radius
approaching a bubble of 100 μm radius

$$\rho_p = 2.5 \text{ gcm}^{-3}$$



CHAPTER 4

RESULTS AND CONCLUSIONS

4.1 Experimental Results

As the flotation results in Section 2.9 were obtained using a Coulter Counter, it was therefore possible to present the change in number of particles with time for individual particle sizes.

Figure 4.1 shows the change in $\ln \frac{N_0}{N}$ with time for different particle sizes as taken from one of the experiments. Here N_0 and N are the number of particles within a particular size range at time = 0 and time = t , respectively. A plot of $\ln \frac{C_0}{C}$ versus time, which enables calculation of the average rate constant is also included in this figure. As it is observed, a straight line can be conveniently fitted through the data points and the assumption of a first order rate for flotation experiments could thus be assumed to hold.

Program COULTER (refer to Section 2.6.3b, Chapter 2) was used in order to convert experimental data into rate constants. Two library subroutines (POLYA and POLYB) were used to calculate the first order rate constant by Least Squares Method. A standard error is quoted for each estimated rate constant.

From Figure 4.1, it is evident that not all the lines pass through zero.

The zero time for each experiment was assumed to correspond to the moment the bubbles were first released at the bottom of the column. A sample corresponding to zero time was taken prior to the bubbles entering the column. The other samples were taken from the recycle stream issuing from the bottom of the column after exact time intervals. There would therefore appear to be no reason for the zero time for experiment and actual zero time to

FIGURE 4.1: $\ln (N_0/N)$ versus time for flotation in distilled water. salt concentration $10^{-2}M$ Na_2SO_4 , surfactant concentration 20 ppm Ethoquad 18/25

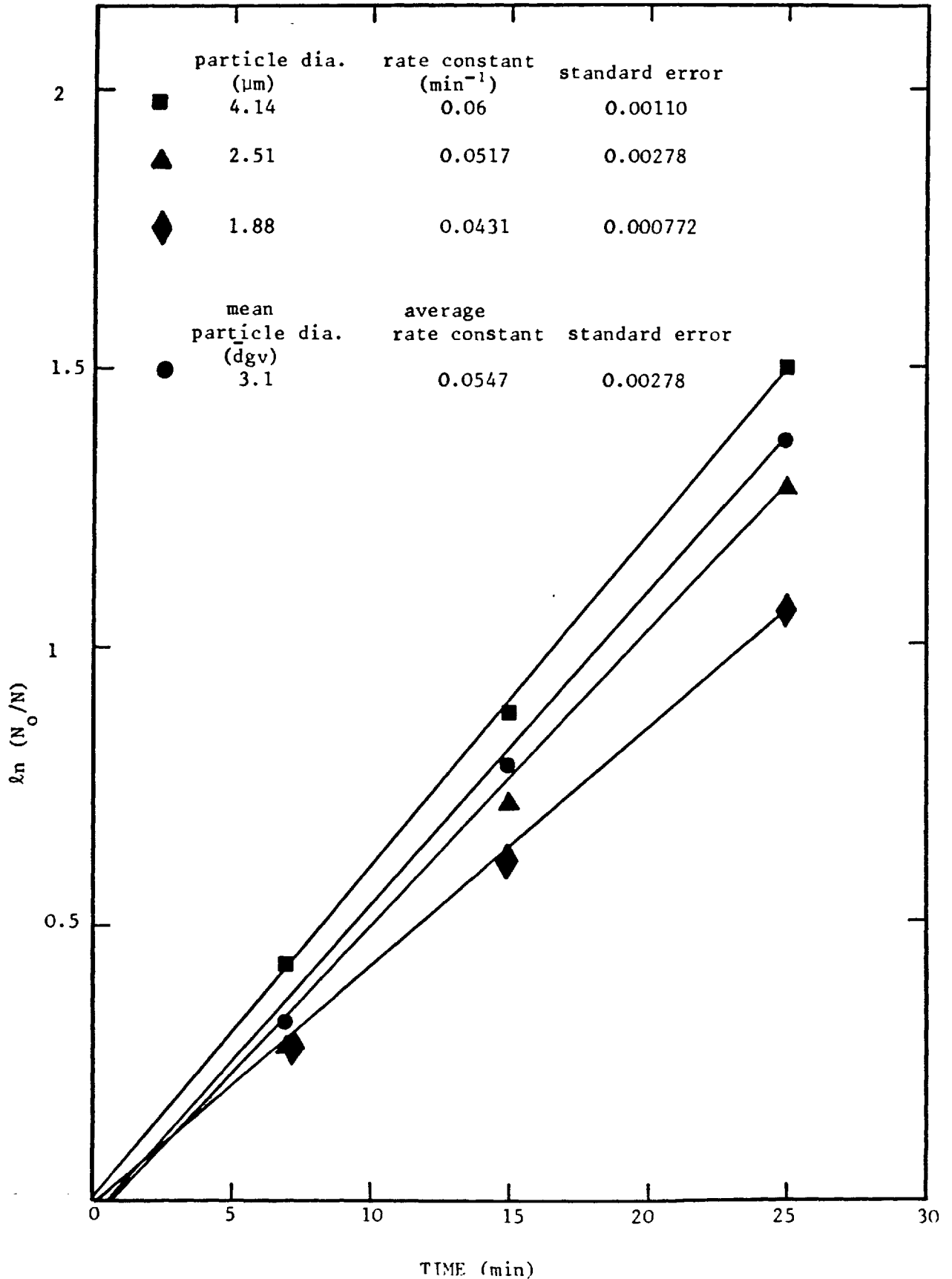
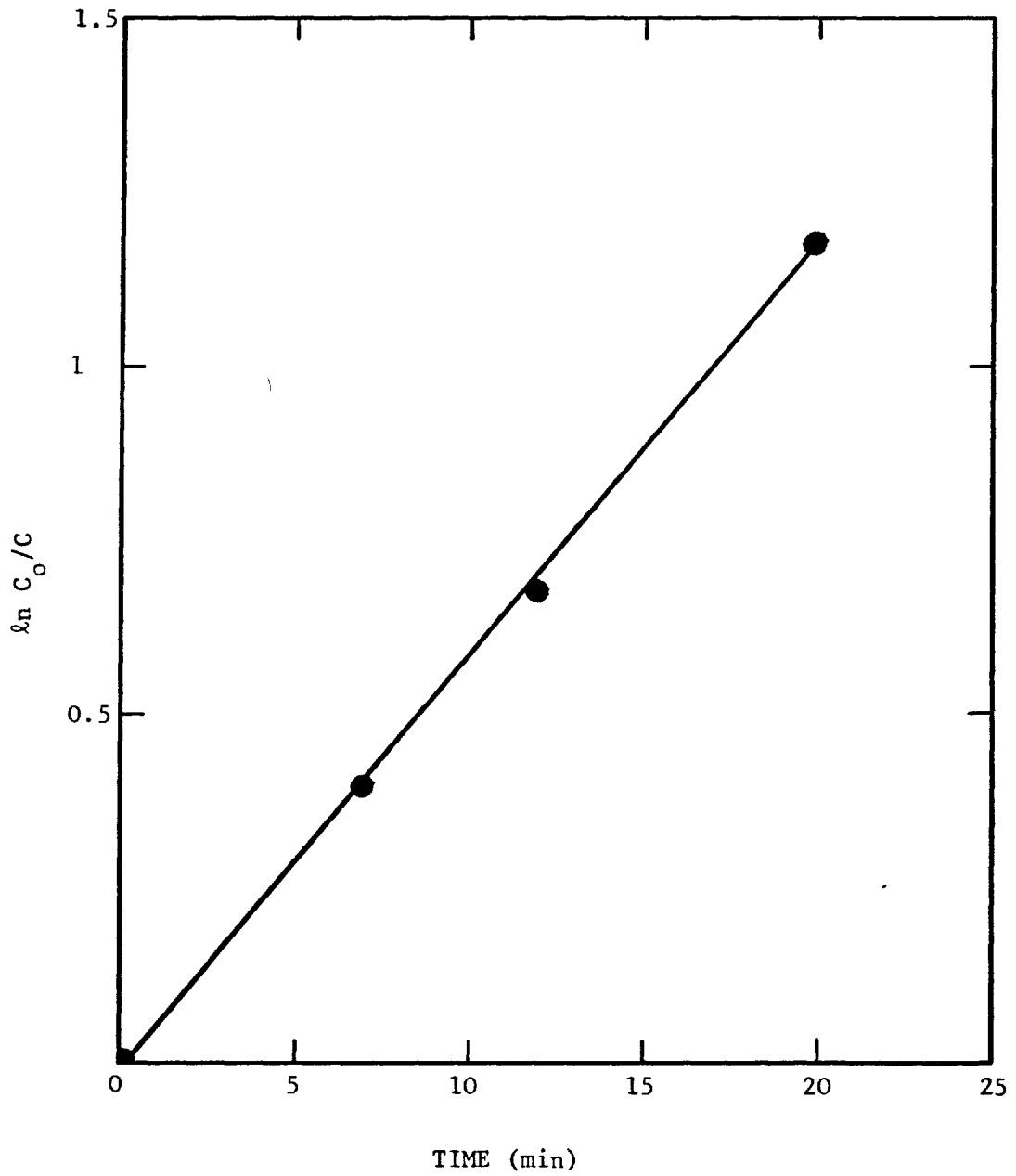


FIGURE 4.2: $\ln C_0/C$ versus time for flotation in tap water, Ethoquad 18/25 20 ppm



differ. This behaviour could be attributed to the error introduced by Coulter Counter in the analysis of the samples. The contribution of the error introduced by cumulative counts on the calculation of rate constant has been discussed by Collins (1975). His analysis showed that a standard deviation of 1 - 2% in the cumulative counts of the Coulter Counter can produce a standard deviation of 10% in the value of $\ln \frac{N_0}{N}$ and therefore on the rate constant. He also mentioned the case where $\ln \frac{N_0}{N}$ was negative as another serious source of error arising from Coulter Counter measurements. This situation rarely occurred in the measurements carried out in this work.

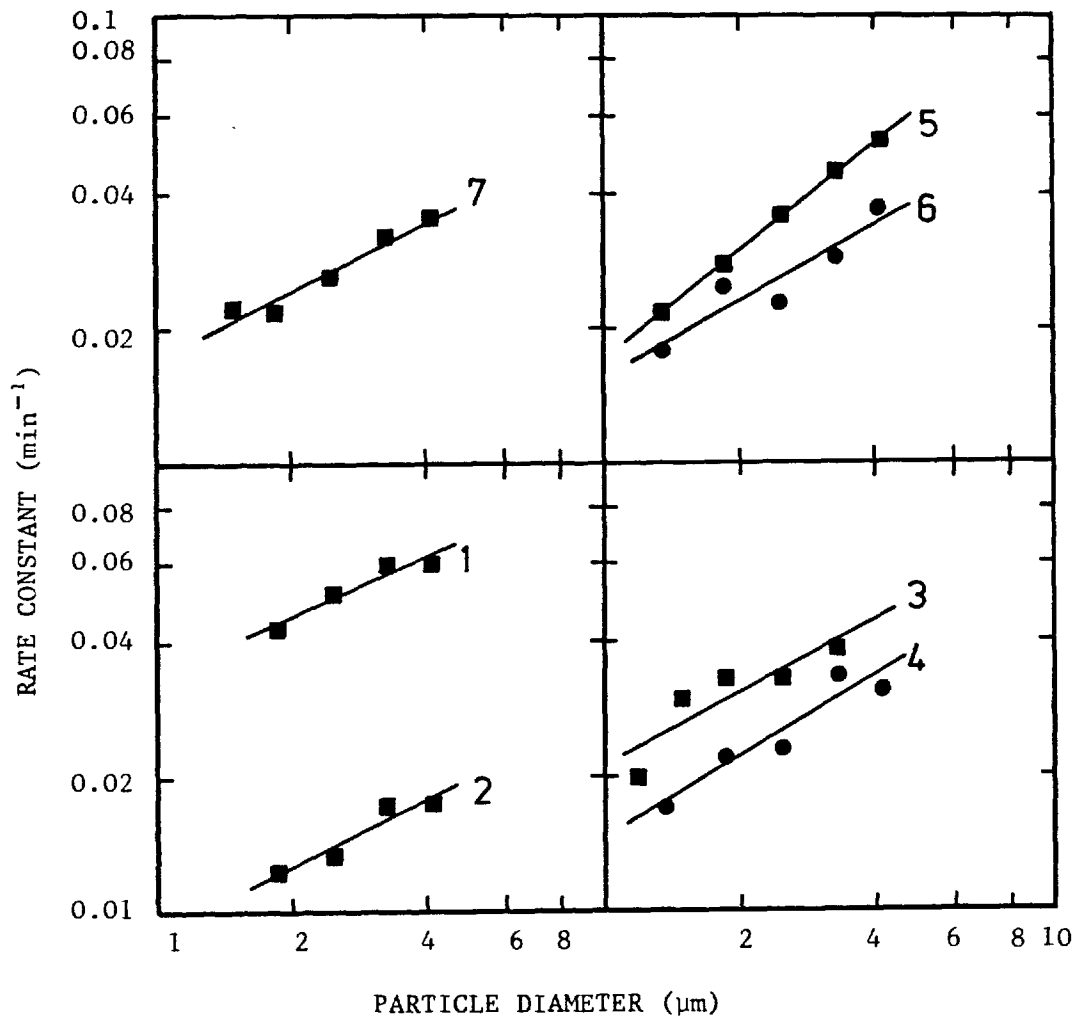
However, introduction of corrections for zero time accounted for a difference of less than three per cent in the values of the calculated slopes. The error was regarded as negligible and no corrections were introduced in subsequent evaluation of rate constants. Similar plots to that of Figure 4.1 were constructed for the rest of the experiments.

A typical plot of $\ln \frac{C_0}{C}$ versus time obtained from experiments carried out with tap water is shown in Figure 4.2. Plots for individual particle sizes are not included, since coagulation which in this case can be regarded as an inevitable process, results in an inaccurate prediction of rate constant for individual sizes.

4.1.1 Dependence between Rate Constant and Particle Size

With the rate constants, k , obtained as discussed above, a plot of k versus particle size on a log scale has been constructed for each experiment. Some of these plots are shown in Figure 4.3 for different experiments, and it is observed that the data points

FIGURE 4.3: Rate constant versus particle size for different flotation experiments



can be adequately fitted by a straight line. The conditions for each of these experiments as well as the slope of best line, q , fitted through the points, are given in Table 4.1.

TABLE 4.1: Values of q in the Relation $k \propto d_p^q$ for Different Experiments

	Salt concentration Na_2SO_4 , $\text{M}\ell^{-1}$	Surfactant concentration Ethoquad, ppm	pH	Gas flowrate $\text{cm}^3 \text{ min}^{-1}$	q
1	10^{-2}	20	9.1	150	0.44
2	5×10^{-5}	20	9.1	150	0.51
3	2×10^{-3}	20	8.3	150	0.51
4	2×10^{-3}	20	6.95	150	0.60
5	2×10^{-3}	30	9.1	150	0.80
6	2×10^{-3}	40	9.1	150	0.56
7	2×10^{-3}	20	6.95	138	0.50

The value of q varies between 0.44 and 0.8, but for most of the experiments it is about 0.5. The following relation representing the dependence between rate constant and particle size can be therefore suggested,

$$k \propto d_p^{0.5} \quad (4.1)$$

4.1.2 Dependence between Rate Constant and Bubble Size

Due to the limited number of experiments performed for this particular purpose, predictions on the basis of plots similar to Figure 4.3 for rate constant versus bubble size were regarded as unreliable. The few experimental results given in Section 2.9.7 of Chapter 2 are later on examined to provide a check on

theoretical prediction of rate constant on bubble size.

4.2 Theoretical Results

As a first attempt to calculate the collision efficiency for a bubble-particle system using the procedure developed in Chapter 3, curves of efficiency versus parameters G_F and K_F used by Flint and Howarth (1971) were constructed. These parameters as given in Chapter 1 are,

$$K_F = \frac{2\rho_p r_p^2 U}{9\mu r_b} \quad ; \quad G_F = \frac{2(\rho_p - \rho_f) r_p^2 g}{9\mu U}$$

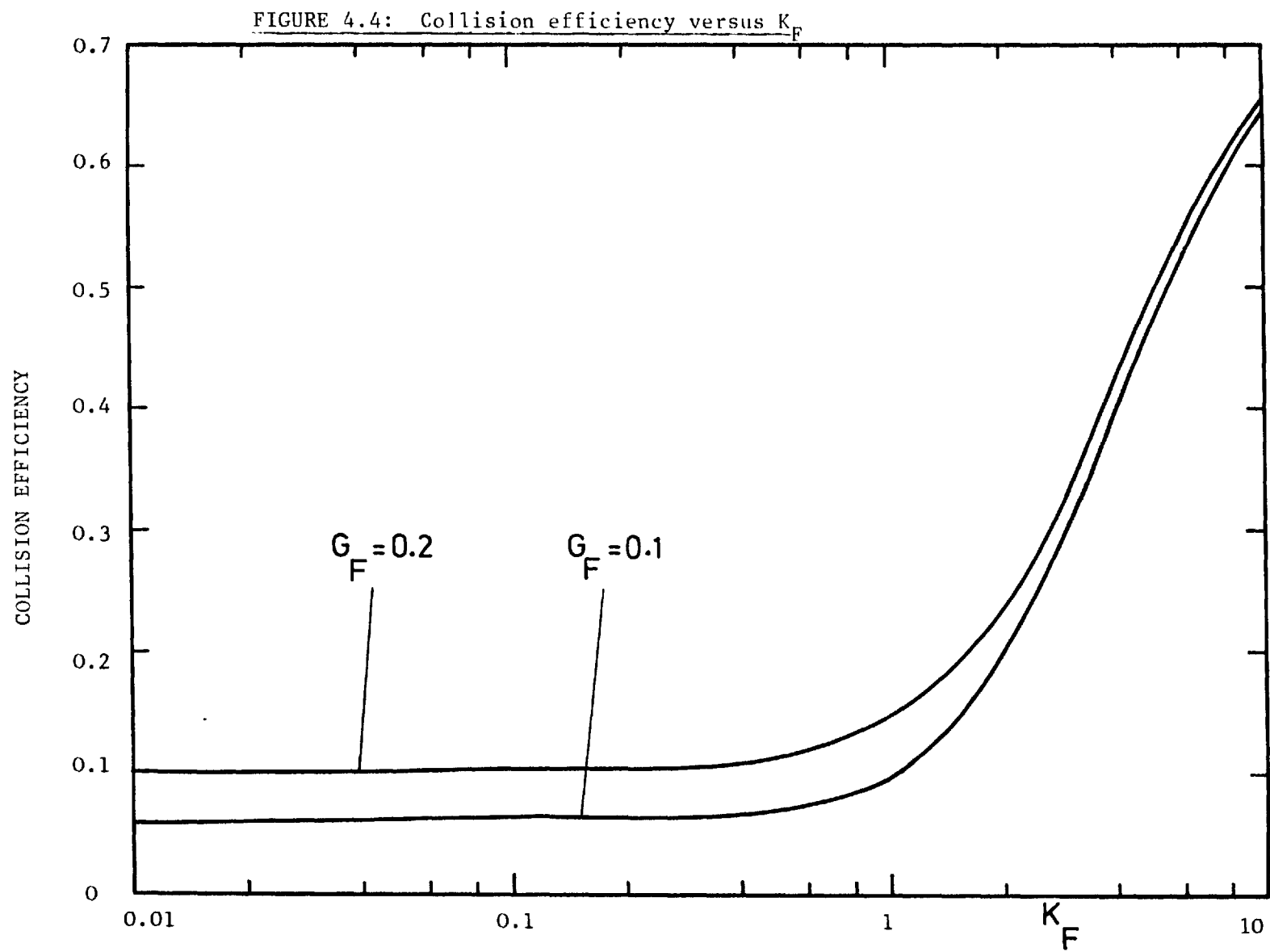
As also mentioned before, the following definition is used for collision efficiency of a single bubble,

$$E_c = \frac{Y_\infty^2}{(1+RA)^2} \quad (4.2)$$

where Y_∞ is obtained as described in Section 3.5.1, Chapter 3. and RA is the ratio between the radii of particle and bubble.

Figure 4.4 shows the variation in E_c as a function of K_F for two different values of G_F . The curves show the same general tendency as those of Flint and Howarth. However, the results, especially for K_F below 3, are drastically lower than their prediction. The discrepancy can be attributed to their definition of collision efficiency as well as to the hydrodynamic correction introduced in the present work.

A comparison can also be made with the results obtained by Reay and Ratcliff (1973) for particle densities of 2.5 gcm^{-3} . Their definition of collision efficiency is the same as that used in this work. The results obtained are again much lower than those produced by these authors (Figure 4.5). Therefore, it can be concluded that the collision efficiency is certainly



lower when hydrodynamic corrections are introduced to the equations of motion. This, in fact, contradicts the theoretical predictions of Collins and the arguments put forward to justify the higher efficiencies obtained through his model (Jameson et al, 1977).

The dependence of efficiency on particle size as calculated in this work for the range of particles shown in Figure 4.5 ($d_b = 100 \mu\text{m}$) is,

$$E_c \propto d_p^{1.5} \quad (4.3)$$

The power of d_p calculated by Reay and Ratcliff for the same system is 2.05.

There are almost no theoretical results available on collision efficiency of buoyant particles. In order to compare the collision efficiency of a buoyant particle, $\rho_p = 0.73 \text{ gcm}^{-3}$, to that of a heavy particle, $\rho_p = 2.5 \text{ gcm}^{-3}$, the grazing trajectory of a $20 \mu\text{m}$ particle approaching a $100 \mu\text{m}$ bubble was determined theoretically. The results are given below,

$$E_c = 0.025$$

$$\rho_p = 0.73$$

$$E_c = 0.04$$

$$\rho_p = 2.5$$

These results show a difference of 40% in collision efficiency for these two systems.

To enable comparisons with other available theoretical models, the results reported above did not account for the effect of interaction due to intermolecular forces.

FIGURE 4.5: Collision efficiency versus particle to bubble size ratio, $\rho_p = 2.5 \text{ gcm}^{-3}$

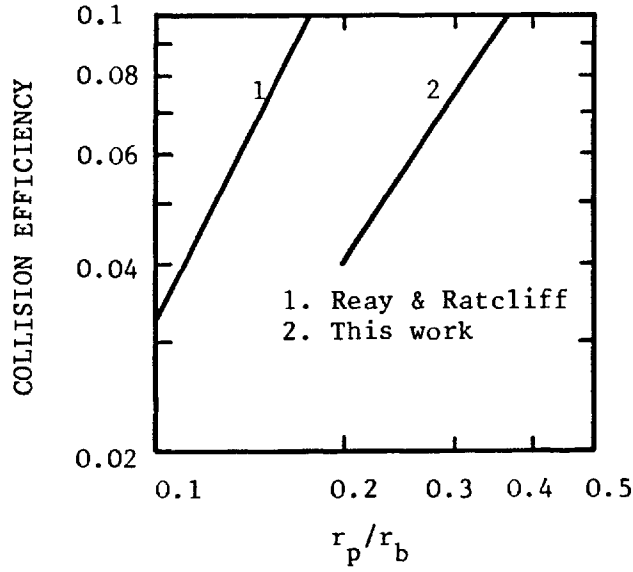
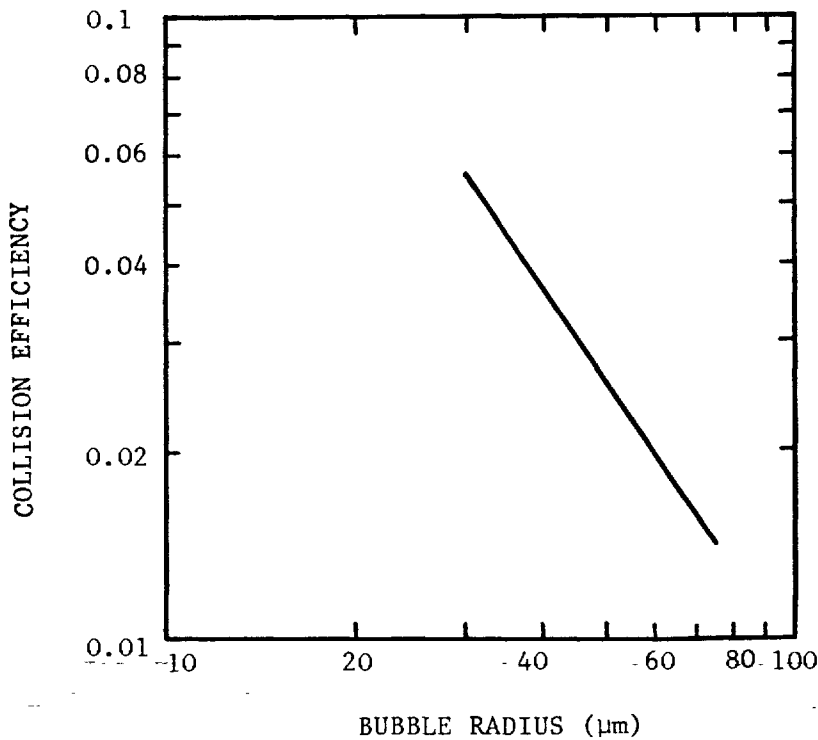


FIGURE 4.6: Collision efficiency versus bubble size, $r_p = 10 \text{ }\mu\text{m}$, $\rho_p = 0.73 \text{ gcm}^{-3}$



4.2.1 Dependence between E_c and Bubble Size

For this part, the calculation of efficiency was carried out considering an oil particle-bubble system. Both repulsion and attraction forces were incorporated in the equations of motion. The Hamaker constant for the oil (n-decane)-water-air system and the calculation of ζ potential from electromobility data are reported in Section 3.3.4, Chapter 3.

The electromobility of the bubbles was arbitrarily taken equal to the particles.

The integration of trajectory for this system was a tedious and highly time-consuming procedure, since a large number of integration steps was necessary. Therefore, problems of accuracy arose due to accumulation of errors introduced by calculation of differences of very small numbers at each step. Difficulties in computation did not practically allow to proceed the calculation of trajectory for surface-surface separations below 500 nm. The effect of intermolecular forces, as can be observed in Figure 3.7, Chapter 3, becomes more pronounced when the distance between the surfaces is around 50 nm. Therefore, it was not possible to assess exactly the effect of attractive and repulsive forces on collection efficiency.

The problems arising in numerical integration of equations of motion when the value of parameter K_F (refer to Figure 4.4) is small, have been also pointed out by Flint and Howarth (1971). The problem is more grave in the case of this work where at any integration step the values of correction factor for Stokes drag term should also be calculated.

For a concentration of salt similar to those employed in the actual flotation experiments, the contribution of intermolecular

forces (including attraction and repulsion) was observed to be always weakly attractive.

The results for efficiency versus bubble size for an oil particle of 10 μm radius is given in Figure 4.6. The dependence between the efficiency and bubble size is obtained as,

$$E_c \propto d_b^{-1.5} \quad (4.4)$$

4.3 Discussion

To compare the experimental results with those obtained from theory, the collection efficiency for a single bubble should be first calculated for the actual flotation system. In most of the experiments performed the average particle diameter lay between 3 - 3.5 μm and the average bubble size was around 300 μm .

Before finding the grazing trajectory for such a system, which was difficult to obtain, the trajectory of a 20 μm oil particle approaching a bubble of 150 μm was obtained numerically.

The result was compared with those obtained through simplified models.

In one case, the grazing trajectory for this same system is calculated on the assumption that the particle follows the fluid streamline.

The fluid stream function for Stokes flow around a bubble of radius R_b is (Bird, Stewart and Lightfoot, 1960),

$$\psi = \frac{1}{4} U_b R_b^2 \sin^2 \theta \left(\frac{R_b}{r} - \frac{3r}{R_b} + 2 \frac{r^2}{R_b^2} \right) \quad (4.5)$$

where U_b is the bubble terminal velocity and r and θ are the fluid particle polar coordinates, with the reference frame $(0, \theta)$ placed on the centre of the bubble.

In the second case, the components of fluid velocity are corrected for the weight of the particle to find the particle streamline. Introducing this correction, the particle stream function is obtained as follows,

$$\psi = \frac{1}{4} U_b R_b^2 \sin^2 \theta \left[\frac{R_b}{r} - \frac{3r}{R_b} + 2(1+G_F) \frac{r^2}{R_b^2} \right] \quad (4.6)$$

where G_F has already been defined.

To find the initial position, y_∞ , for a grazing trajectory, the polar coordinates r and θ in equations (4.5) and (4.6) can be given in terms of the corresponding cartesian coordinates x and y . Therefore,

$$r = (x^2 + y^2)^{\frac{1}{2}} \quad \text{and} \quad \sin \theta = \frac{y}{(x^2 + y^2)^{\frac{1}{2}}}$$

For the grazing trajectory, the stream function should satisfy,

$$\begin{aligned} x = 0 & & y = R_b + r_p \\ y \rightarrow \infty & & y = y_\infty \end{aligned}$$

Applying these two conditions to the above expressions, the value of y_∞ can be calculated.

The efficiencies obtained from different methods are given in Table 4.2.

TABLE 4.2: Collision efficiency for a bubble and an oil particle

$$\underline{d_p = 20 \text{ } \mu\text{m}, d_b = 150 \text{ } \mu\text{m}.}$$

	single bubble efficiency, E_c
exact solution	0.0142
equation (4.5)	0.0190
equation (4.6)	0.0152

These results clearly show that one could safely use the particle stream function to calculate the efficiency in a system where the ratio of bubble to particle size is sufficiently large.

Considering a typical case of actual flotation experiments,

$$d_p = 3.2 \text{ } \mu\text{m}$$

$$d_b = 330 \text{ } \mu\text{m}$$

$$\rho_p = 0.73 \text{ gcm}^{-3}$$

The efficiency can therefore be calculated on the basis of approach described above. The results are,

$$E_c = 0.00014$$

(equation 4.5)

$$E_c = 0.000113$$

(equation 4.6)

To compare the single bubble efficiency obtained above with other available models, the efficiency for the same system was calculated using Prieve and Ruckenstein's model (1974). They presented their results in the form of plots of Sh number versus Pe number for different aspect ratios, $Ra = r_c/r_p$, and different values of attraction, A/KT .

Using one of their curves corresponding to neutrally buoyant particles and selecting the nearest A/KT and Ra to the system considered in the present work, both Sh and Pe numbers can be determined. Therefore,

$$T = 295^{\circ} \text{K}$$

$$Pe = 1.449 \times 10^8$$

$$Sh = 2.9 \times 10^3$$

According to their definition for the efficiency of a single

sphere,

$$E = 4 \frac{Sh}{Pe} = 8 \times 10^{-5}$$

which is almost in agreement with the value obtained before from equation (4.6).

Using the following correlation between E and the average rate constant, k , as given by Jameson et al (1977) for a batch flotation system, E can be determined experimentally (refer to equation (1.5), Chapter 1).

$$k = \frac{3Q}{2} \frac{E}{d_b} \frac{h}{V_c} \quad (4.7)$$

Applying data from one of the experiments carried out in this work to the above equation,

$$Q = 150 \text{ cm}^3 \text{ min}^{-1}$$

$$h = 78.5 \text{ cm}$$

$$d_b = 330 \times 10^{-4} \text{ cm}$$

$$V_c = 5500 \text{ cm}^3$$

$$k = 0.04 \text{ min}^{-1}$$

the following value of E is obtained

$$E = 0.00041$$

which is much higher than the values produced theoretically.

Higher predictions for E are however expected from (4.7) when experimentally measured k are used. The reason lies in the fact that in actual experiments a swarm of bubbles is produced which could affect the capture efficiency in different ways, such as,

- a) In an assemblage of bubbles, the bubble rising velocity,

relative to the liquid, is reduced due to the hindering effects of neighbouring bubbles. Therefore, its residence time within the column increases as well as its probability of collecting more particles.

- b) The residence time of the bubbles can also be increased by turbulence induced in the flotation column.
- c) It is known that spheres in an assemblage tend to straighten the streamlines of the neighbouring spheres, a fact which also enhances collision efficiency.
- d) The motion of particles at large distances upstream of a bubble is affected by the bubbles ahead of it and is no longer parallel to the direction of bubble motion.

This behaviour could also affect collision efficiencies.

In order to assess the effect of repulsion forces on the collection efficiency, a semi-empirical correlation was employed. According to the analysis of Spielman and Fitzpatrick (1973) and their experimental results (Fitzpatrick and Spielman, 1973), double layer repulsion can be regarded as negligible if the following inequality is satisfied,

$$\left(\frac{N_{\zeta}}{\tau} \right) (N_{Ad} \tau^2) \times \frac{\exp(-N_{Ad}^{\frac{1}{2}} \tau / 4.41)}{1 + \exp(-N_{Ad}^{\frac{1}{2}} \tau / 4.41)} < 1.0 \quad (4.8)$$

where,

$$N_{Ad} = \frac{Ar_c^2}{9\pi\mu_c U_{r_p}^4} ; \quad N_{\zeta} = \frac{3\epsilon\zeta_1\zeta_2 r_p}{2A} ; \quad \tau = \kappa r_p$$

and ζ_1 and ζ_2 are the ζ potentials corresponding to collector and particle.

For a typical system considered in this work,

$$r_p = r_c = 165 \times 10^{-4} \text{ cm}$$

$$r_p = 1.6 \times 10^{-4} \text{ cm}$$

$$A = 10^{-13} \text{ ergs}$$

$$\zeta_1 = \zeta_2 = 31 \text{ mV}$$

$$\text{salt concentration} = 2 \times 10^{-3} \text{ M}\ell^{-1}$$

The dimensionless values, N_{Ad} , N_ζ and τ are obtained as follows,

$$N_{Ad} = 2.476 \times 10^{-2}$$

$$N_\zeta = 2000$$

$$\tau = 409.$$

Applying these values in the above inequality,

$$\text{L.H.S.} = 0.01$$

which shows that repulsion for the system under consideration is negligible. Changing the concentration of salt in the above system to 5×10^{-4} and 5×10^{-5} alters the L.H.S. of (4.8) to 13 and 635, respectively. In other words, this indicates that the charge affects the collection efficiency for these two last systems. This is in agreement with the experimental results of Section 2.9.6, Chapter 2, where the average rate constant drops as the electromobility of the particles increases with the other variables kept constant.

In order to compare the effect of bubble size on the rate constant as predicted from theory and experiments, E from correlation (4.4) which is theoretically obtained can be replaced in (4.7). The following dependence between k and d_b can thus be obtained.

$$k \propto d_b^{-2.5} \quad (4.9)$$

The experimental results of Section 2.9.7, Chapter 2, can now be used to test the above theoretical correlation.

Thus, using the following sets of experimental data, i.e.

Set 1	Set 2
$d_{b1} = 388 \mu\text{m} \quad k_1 = 0.0588 \text{ min}^{-1}$ $d_{b2} = 328 \mu\text{m} \quad k_2 = 0.0848 \text{ min}^{-1}$	$d_{b1} = 322 \mu\text{m} \quad k_1 = 0.064 \text{ min}^{-1}$ $d_{b2} = 312 \mu\text{m} \quad k_2 = 0.069 \text{ min}^{-1}$

The corresponding powers in correlation (4.9) are found to be 2.2 and 2.4 for the first and second set, respectively.

Although expression (4.9) was obtained for bubble sizes lower than $150 \mu\text{m}$, the agreement between theory and experiments for bubble sizes larger than $300 \mu\text{m}$ is satisfactory.

To check the dependence between E and particle size for the range of sizes of interest to this work, the theoretical results of Prieve and Ruckenstein (1974) for buoyant particles were considered. Replotting their results of ERa^2 versus Pe/Ra^3 for different aspect ratios, it was found that ERa^2 was only a function of Pe/Ra^3 for values of this parameter greater than 10 (Figure 4.7).

Therefore,

$$E Ra^2 \propto \left(\frac{Pe}{Ra^3} \right)^N \quad (4.10)$$

$\frac{Pe}{Ra^3}$ can be written as

$$\frac{Pe}{Ra^3} = \frac{8\pi g \Delta \rho r_p^4}{3KT}$$

Consider the following system,

$$r_p = 1.6 \times 10^{-4} \text{ cm}$$

$$r_b = 165 \times 10^{-4} \text{ cm}$$

$$T = 295^{\circ} \text{ K}$$

$$\Delta\rho = \rho_f - \rho_b = 0.9988 \text{ gcm}^{-3}$$

This gives,

$$\frac{Pe}{Ra^3} = 132$$

The slope of the graph at this value of $\frac{Pe}{Ra^3}$ is, -0.176 .

Therefore,

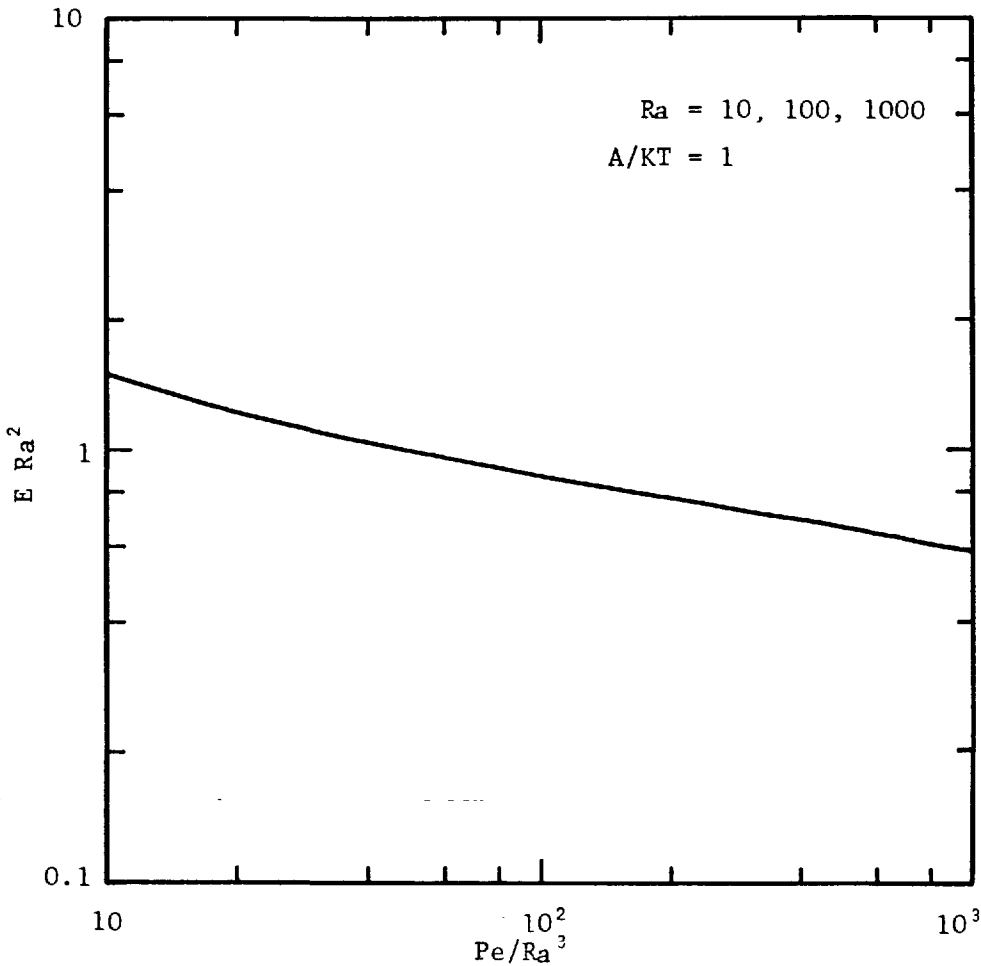
$$E Ra^2 \propto \left(\frac{Pe}{Ra^3} \right)^{-0.176}$$

or

$$E \propto \frac{d_p^{1.3}}{d_b^2} \quad (4.11)$$

Comparing this to the experimental result of $E \propto d_p^{0.5}$ obtained here, their prediction appears to over-estimate the dependence of E on d_p .

FIGURE 4.7: Plot of $E Ra^2$ vs. Pe/Ra^3 for different aspect ratios, Ra , produced from Sh-Pe plots calculated by Prieve and Ruckenstein (1974)



As only attractive forces have been taken into account in the theoretical model, one possible reason for such a discrepancy should be sought in the effect of repulsive double layer forces. This conclusion is based on the experimental findings of this work and pointed out in Section 2.10.

The theoretical approach developed in previous chapters to evaluate collision efficiencies offers further refinements to previous hydrodynamic theories available in the literature on both filtration and flotation processes. Thus, exact solutions for the hydrodynamic corrections to the viscous drag, within the limitation of the creeping flow approximation, have been incorporated to the equations of motion of a system of two spheres of any arbitrary relative size approaching each other. Corrections to allow for retardation of intermolecular attraction forces have also been taken into account. The general results obtained here are therefore also of interest to workers in related fields such as coagulation and coalescence.

When applied to the evaluation of grazing trajectories, however, the approach faces unavoidable difficulties associated with the highly time consuming computational procedure required at close distances of separation between particles. Thus, although trajectories can in principle be satisfactorily carried out, it becomes impractical to proceed with integration for separation gaps below about 500 nm. As a consequence, it is difficult to assess the effect of double layer repulsion forces which, for the systems of interest to this work become operative within this range of distances.

Further theoretical work could be suggested on the lines of Spielman and Cukor's (1973). For the particular case of a small particle to bubble size ratio, the bubble trajectory can be safely

assumed to be unaffected by that of the particles. Also, provided that a balance between hydrodynamic, attractive and repulsive forces on the particle, as derived in this work, gives rise to a stagnation point at the rear of the bubble, only one trajectory need be evaluated to calculate collision efficiencies. However, whatever the approach used, there seems at this stage to be little point in sophisticating hydrodynamic models any further, unless the role of intermolecular forces is elucidated, in particular that of the specific surface forces arising in water-dispersed systems.

On the experimental side, some typical values obtained in the present work for removal % as defined by the following expression are reported in Table 4.3.

$$R = \frac{C_o - C}{C_o} \times 100$$

where C_o and C are the concentration of particles at time = 0 and time = t , respectively.

TABLE 4.3: Percentage of oil removal in the flotation column for different experiments. pH 9.1, Q 150 cm³ min⁻¹ duration of experiment t = 25 min.

Na ₂ SO ₄ Mℓ ⁻¹	R
5×10^{-5}	37
5×10^{-4}	42
10^{-2}	75
10^{-1}	81
0.28	86
tapwater *	81

* pH 8.1, duration of experiment 20 min.

These values cannot be compared to other data available on the flotation of oil particles in literature, mainly due to unavailability of reliable data for the range of particle sizes studied in this work. In this context, it should be pointed out that the particle size in a dissolved air flotation chamber is typically in the range of 10 - 100 μm .

Some of the lines, along which further improvements on the performance of the dispersed air flotation system employed in this work could be achieved, are

- a) Further modifications could be introduced in the bubble generation device in order to obtain lower bubble size distributions.
- b) A suitable gas flowrate should be found to provide adequate population of small bubbles in the column while simultaneously minimising the amount of foamate formed.
- c) A better choice of surfactant could be found to assist in both the reduction of bubble size and of bubble-particle repulsion.

APPENDICESAPPENDIX 1Different Techniques tried for Preparation of Emulsion1. Simple Stirrer

The first method used to prepare the emulsion consisted of stirring the mixture of oil and water in a large beaker, by means of a simple stirrer. A certain amount of a surface active agent, planned to be used in the experimental work, was added to the water. Mixing was carried on for 40 minutes during which samples were taken and immediately analysed under a microscope provided with a calibrated eyepiece graticule. No obvious change in droplet size was observed after 20 minutes. However, a very thin layer of emulsified oil tended always to form at the interface. The size range of the distribution was rather broad and the particle size lay invariably between 1 to 30 μm .

2. High Speed Stirrer

The next device tried was a laboratory mixer emulsifier (Silverson Machines Ltd), with a variable speed control. Different speeds of stirrer were chosen and mixtures were emulsified for 30 minutes.

Although the particle size range was narrower than before, the big particles tended always to coalesce to form a thin layer of oil at the top of the vessel. It was therefore concluded that a suitable emulsion could never be achieved through this method.

3. Ultrasonic Emulsifier-Stirrer

To prepare the emulsion using an ultrasonic emulsifier, the oil was first poured into one of the glass vessels of the machine. Water was next added and emulsification started. While the liquid was

continuously recycled into the vessel, a simple stirrer was used to keep the solution mixed. The operating pressure of the pump was kept at about 165 psi (the normal working condition). The emulsion was prepared with or without surface active material. In different runs, a time for emulsification of up to 5 minutes was allowed. Samples were taken at two minutes intervals and examined under the microscope.

The particles formed in the presence of surfactant looked comparatively smaller. In fact, most of them looked well below 1 μm . Therefore, it was decided to prepare the emulsion without any surface active agent added to the water. A time for emulsification of 5 minutes was chosen, as after this time a rather suitable emulsion was obtained. Shorter times results in the appearance of unemulsified oil drops on the surface. In some of the preliminary flotation experiments, the emulsion was prepared in this way.

As the particle size was hardly ever larger than 3 μm and mostly lay in the order of about 1 μm , it was decided to change the emulsification technique to be able to raise the size to a sensible level (3 - 8 μm) from the point of view of flotation experiments. Thus, several other experiments were carried out using a combination of the high speed stirrer and the ultrasonic emulsifier as well as shorter intervals of time. The results were not considerably different from previous results.

4. Ultrasonic with Reduced Pressure-Stirrer

Emulsification efficiency increases with the velocity of the liquid jet stream in the ultrasonic emulsifier, and this velocity is directly related to the pump pressure. Therefore, a decrease in

the pump pressure would be expected to decrease the emulsification efficiency, and would probably result in larger particle size. On this basis, several experiments were performed under different pump pressures. To enable a precise measurement of pressure, the manometer provided with the instrument by the manufacturer was replaced by a more precise one, of working range 0 - 500 psi.

The pressure was varied between 100 - 150 psi. Although the average particle size was shifted towards a bigger value, few un-emulsified drops were still observed at the surface of the emulsion. A stirrer was always used to provide mixing in the container of the emulsifier. In cases where lower pump pressures (100 - 120 psi) were involved, the high speed stirrer was used for mixing. Here, it was observed that a minimum emulsification time of 4 minutes was required to obtain a rather reasonable emulsion. Smaller intervals of time, i.e. 2 minutes, resulted in a broad droplet size distribution with more unemulsified oil at the top.

On the whole, the results were not satisfactory, and it was decided that some modification on the emulsifier itself was warranted.

5. Modified Ultrasonic Emulsifier

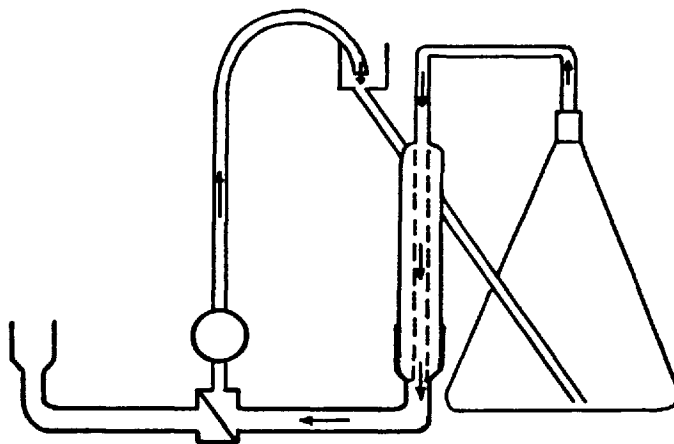
This system is shown in Figure A1.1. The main reason for devising such a system was to enable liquid to be drawn from the top of the emulsion, while simultaneously facilitating its continuous passage through the pump and homogeniser head. In the previous methods, even when mixing was always provided, and due to the fact that liquid was sucked into the pump from the bottom part of the vessel, the possibility remained that part of the oil might never pass into the emulsification section. The modified part for the emulsifier was made entirely out of glass, and it was designed in order to fit that

part of the apparatus where the container of the emulsifier was supposed to be placed. The oil and water were premixed with a simple stirrer, in a separate vessel for 2 to 5 minutes. The mixture was then poured into the conical part through a funnel until the system was filled up with liquid.

Several experiments were performed, choosing different times (1 - 5 minutes) and pressures of emulsification (100 - 170 psi). Unfortunately, the method was not successful as part of the oil left behind on tubings walls and other parts of the glass vessel, produced a layer of oil on the top of the final emulsion. Longer times of emulsification, i.e. 4 to 5 minutes, led to smaller particles with still some drops of unemulsified oil present.

A suitable technique was eventually found using the ultrasonic emulsifier. The details have been given in Section 2.4.2.

FIGURE A1.1: Modified ultrasonic emulsifier



APPENDIX 2

Bubble Photography Devices

To photograph the bubbles, different types of flat cells were designed as described below.

1. Square Cell

As a first attempt, a $1.5 \times 1.5 \times 5$ cm square cell was used.

Photographs taken at different parallel planes across the flat cell appeared blurred. In other words, interference due to the large population of bubbles within the cell prevented a sharply defined picture of the bubbles from being obtained.

2. Branched Square Cell

To overcome the difficulty mentioned above, a design similar to Figure A2.1 was tried. The flat cell had a 1×1 cm cross section and the branched section was a circular tube of 0.5 cm diameter. Thus, the light path of the square cell described in (1) was comparatively reduced. The branched section was employed in order to cut the population of the bubbles in the cell.

The square part was found to be suitable for photography but coalescence in the branched section due to the bends, affected the bubble size distribution.

Finally, a rectangular cell was found to be the most adequate. The details have been given in Section 2.5.

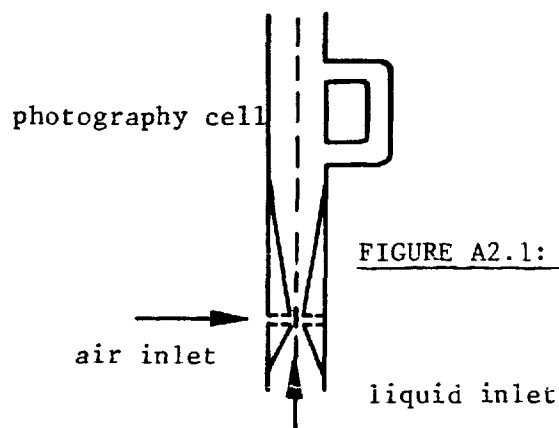


FIGURE A2.1: The modified photography set-up

APPENDIX 3Settings for the Coulter Counter

Different settings used for the Coulter Counter are given in Table A3.1. The corresponding diameters are calculated using a calibration factor of 1.0724.

TABLE A3.1: Coulter Counter Settings

Lower threshold setting t_i	1/aperture current setting I	1/amplification setting A	diameter μm	mean diameter in range μm
25	4	16	12.54	11.25
25	4	8	9.95	8.93
25	4	4	7.90	7.09
25	4	2	6.27	5.78
30	2	2	5.29	4.95
20	2	2	4.62	4.14
20	1	2	3.66	3.29
20	1	1	2.91	2.50
15	$\frac{1}{2}$	1	2.1	1.88
15	$\frac{1}{2}$	$\frac{1}{2}$	1.66	1.49
15	$\frac{1}{2}$	$\frac{1}{4}$	1.32	1.18
15	$\frac{1}{2}$	$\frac{1}{8}$	1.05	0.98
10	$\frac{1}{2}$	$\frac{1}{8}$	0.92	

APPENDIX 4The Bipolar Coordinates (ξ, η, ϕ)

Bipolar Coordinates (ξ, η) in a plane are defined by the transformation

$$z + i\rho = ic \cot \frac{1}{2}(\eta + i\xi) \quad , \quad c > 0 \quad (1)$$

Therefore,

$$z = c \frac{\sinh \xi}{\cosh \xi - \cos \eta} \quad , \quad \rho = c \frac{\sin \eta}{\cosh \xi - \cos \eta} \quad (2)$$

Considering that

$$0 \leq \eta \leq \pi, \quad -\infty < \xi < \infty, \quad 0 \leq \phi < 2\pi$$

each point in space is therefore represented only once in this system of coordinates. Eliminating η in (2), the following expression is obtained

$$(z - c \coth \xi)^2 + \rho^2 = c^2 \operatorname{csch}^2 \xi \quad .$$

The coordinate surfaces $\xi = \text{constant}$ are, thus, a family of non-intersecting coaxial spheres whose centres lie along the z axis.

For $\xi < 0$ the spheres are below this plane. As ξ decreases from $+\infty$ to 0, the radius of the corresponding sphere increases from zero to infinity and the centre moves from $z = c$ (limiting point) to $+\infty$.

By eliminating ξ in equation (2),

$$z^2 + (\rho - c \cot \eta)^2 = c^2 \csc^2 \eta \quad .$$

In a meridian plane, the curves $\eta = \text{constant}$ are arcs of circles, terminating at the limiting points of the system (L_1, L_2 , Figure A4.1) having their centres in the plane $z = 0$. Upon rotating these arcs about the z axis, the coordinate surfaces $\eta = \text{constant}$ are

obtained. The value $\eta = 0$ corresponds to the two segments of the z axis which lie above L_1 and below L_2 . $\eta = \pi$ is the line segment between L_1 and L_2 . $\eta = \pi/2$ is a sphere of radius C .

The distance from the origin ($\eta = \pi, \xi = 0$) to a point in space in this system is

$$r = (\rho^2 + z^2)^{\frac{1}{2}} = c \left(\frac{\cosh \xi + \cos \eta}{\cosh \xi - \cos \eta} \right)^{\frac{1}{2}}$$

A typical sphere $\xi = \xi_1$ has its centre at the point ($\rho = 0$, $z = c \coth \xi_1$) and has a radius of $c |\operatorname{csch} \xi_1|$, Figure A4.2.

FIGURE A4.1: Bipolar coordinates

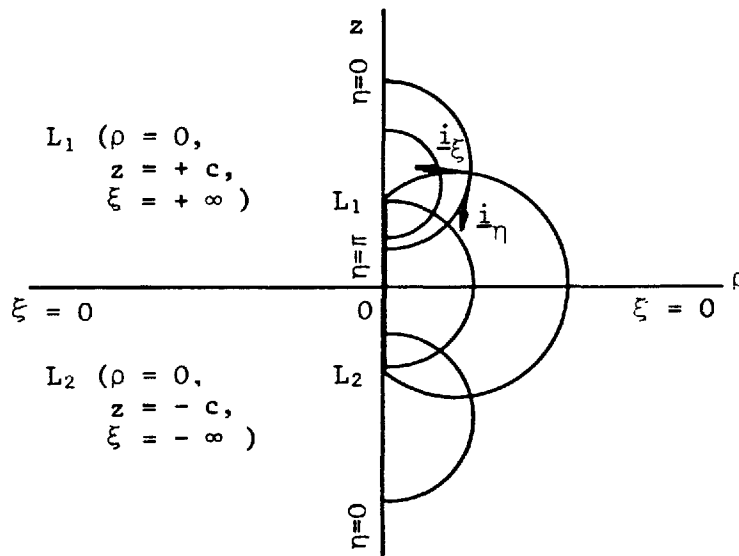
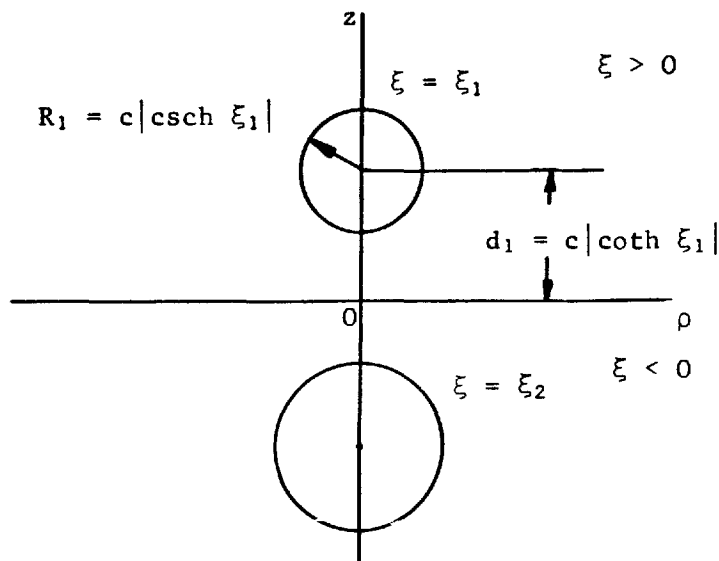


FIGURE A4.2: Spheres in bipolar coordinates



APPENDIX 5Conversion of the Boundary Conditions from Cylindrical Coordinates
into Bipolar Coordinates as used in Section 3.2.1.

The boundary conditions are

$$\left. \begin{aligned} \frac{\partial \psi}{\partial z} &= 0 \\ \frac{\partial \psi}{\partial \rho} &= \rho v_1 \end{aligned} \right\} \text{ on surface of sphere 1}$$

$$\left. \begin{aligned} \frac{\partial \psi}{\partial z} &= 0 \\ \frac{\partial \psi}{\partial \rho} &= -\rho v_2 \end{aligned} \right\} \text{ on surface of sphere 2}$$

Also, by chain differentiation

$$\frac{\partial \psi}{\partial \eta} = \frac{\partial \psi}{\partial z} \frac{\partial z}{\partial \eta} + \frac{\partial \psi}{\partial \rho} \frac{\partial \rho}{\partial \eta}$$

$$\frac{\partial \psi}{\partial \xi} = \frac{\partial \psi}{\partial z} \frac{\partial z}{\partial \xi} + \frac{\partial \psi}{\partial \rho} \frac{\partial \rho}{\partial \xi}$$

The boundary conditions can then be written as follows

$$\left. \begin{aligned} \frac{\partial \psi}{\partial \eta} &= \rho v_1 \frac{\partial \rho}{\partial \eta} = \frac{\partial}{\partial \eta} \frac{1}{2} v_1 \rho^2 \\ \frac{\partial \psi}{\partial \xi} &= \rho v_1 \frac{\partial \rho}{\partial \xi} = \frac{\partial}{\partial \xi} \frac{1}{2} v_1 \rho^2 \end{aligned} \right\} \text{ for } \xi = \alpha$$

$$\left. \begin{aligned} \frac{\partial \psi}{\partial \eta} &= -\rho v_2 \frac{\partial \rho}{\partial \eta} = -\frac{\partial}{\partial \eta} \frac{1}{2} v_2 \rho^2 \\ \frac{\partial \psi}{\partial \xi} &= -\rho v_2 \frac{\partial \rho}{\partial \xi} = -\frac{\partial}{\partial \xi} \frac{1}{2} v_2 \rho^2 \end{aligned} \right\} \text{ for } \xi = \beta$$

or

$$\psi = \frac{1}{2} v_1 \rho^2 \quad \text{at } \xi = \alpha$$

$$\frac{\partial \psi}{\partial \xi} = \frac{\partial}{\partial \xi} \frac{1}{2} v_1 \rho^2$$

and

$$\begin{aligned}\psi &= -\frac{1}{2}v_2\rho^2 \\ \frac{\partial\psi}{\partial\xi} &= -\frac{\partial}{\partial\xi}\frac{1}{2}v_2\rho^2\end{aligned}\quad\text{at }\xi=\beta$$

APPENDIX 6

Obtaining equations (3.38)-(3.40) from the boundary conditions in Section 3.2.2.

$$\text{For sphere 1} \quad \frac{r_1}{c_1} q_1 + u_1 + v_1 = 2U_1 \quad (1)$$

$$u_1 - v_1 = -2U_1 \quad (2)$$

$$\frac{z_1}{c_1} q_1 + 2w_1 = 0. \quad (3)$$

$$\text{For sphere 2} \quad \frac{r_2}{c_2} q_2 + u_2 + v_2 = 2U_2 \quad (4)$$

$$u_2 - v_2 = -2U_2 \quad (5)$$

$$\frac{z_2}{c_2} q_2 + 2w_2 = 0. \quad (6)$$

u_1 , v_1 and q_1 in (1), (2), (3) can be written in term of w_1 as follows

$$u_1 = \frac{r_1}{z_1} w_1 \quad (7)$$

$$v_1 = 2U_1 + \frac{r_1}{z_1} w_1 \quad (8)$$

$$q_1 = -2 \frac{c_1}{z_1} w_1 \quad (9)$$

u_1 , v_1 , q_1 and w_1 can be replaced with the expressions given by (3.29) in Chapter 3.

Equation (7) can be written as

$$\begin{aligned} & (\cosh \xi - t)^{\frac{1}{2}} \sin^2 \eta \sum_{n=2}^{\infty} \left[G_n \cosh(n+\frac{1}{2}) \xi + H_n \sinh(n+\frac{1}{2}) \xi \right] P_u''(t) = \\ & \frac{\sin^2 \eta}{\sinh \xi} (\cosh \xi - t)^{\frac{1}{2}} \sum_{n=1}^{\infty} \left[A_n \sinh(n+\frac{1}{2}) \xi + B_n \cosh(n+\frac{1}{2}) \xi \right] p_n'(t) \quad (7a) \end{aligned}$$

Using the following recurrence formulae

$$P_n'(t) = \frac{1}{(2n+1)} (P_{n+1}''(t) - P_{n-1}''(t))$$

equation (7a) can then be converted as follows

$$\sum_{n=2}^{\infty} \left[G_n \cosh(n+\frac{1}{2}) \xi + H_n \sinh(n+\frac{1}{2}) \xi \right] P_n''(t) =$$

$$\frac{1}{\sinh \xi} \left\{ \sum_{n=2}^{\infty} \left[A_{n-1} \sinh(n-\frac{1}{2}) \xi + B_{n-1} \cosh(n-\frac{1}{2}) \xi \right] \frac{P_n''(t)}{2n-1} - \right.$$

$$\left. \sum_{n=2}^{\infty} \left[A_{n+1} \sinh(n+\frac{3}{2}) \xi + B_{n+1} \cosh(n+\frac{3}{2}) \xi \right] \frac{P_n''(t)}{2n+3} \right\} \quad (7b)$$

After cancelling $P_n''(t)$ and the summations from both sides, equation (3.40) is obtained.

Equation (8) can be written as

$$(\cosh \xi - t)^{\frac{1}{2}} \sum_{n=0}^{\infty} \left[E_n \cosh(n+\frac{1}{2}) \xi + F_n \sinh(n+\frac{1}{2}) \xi \right] P_n(t) = \quad (8a)$$

$$2U_1 + \frac{\sin^2 \eta}{\sinh \xi} (\cosh \xi - t)^{\frac{1}{2}} \sum_{n=1}^{\infty} \left[A_n \sinh(n+\frac{1}{2}) \xi + B_n \cosh(n+\frac{1}{2}) \xi \right] P_n'(t)$$

Using the following expressions

$$\sin^2 \eta \ P_n'(t) = \frac{n(n+1)}{2n+1} (P_{n-1} - P_{n+1})$$

$$(\cosh \xi - t)^{-\frac{1}{2}} = \sum_{n=0}^{\infty} \sqrt{2} \ e^{-(n+\frac{1}{2}) \xi} P_n, \quad \xi > 0$$

and after replacing into (8a) this becomes

$$\sum_{n=0}^{\infty} \left[E_n \cosh(n+\frac{1}{2}) \xi + F_n \sinh(n+\frac{1}{2}) \xi \right] P_n(t) =$$

$$\frac{1}{\sinh \xi} \left\{ \sum_{n=0}^{\infty} \left[A_{n+1} \sinh(n+\frac{3}{2}) \xi + B_{n+1} \cosh(n+\frac{3}{2}) \xi \right] \frac{(n+1)(n+2)}{(2n+3)} P_n(t) \right.$$

$$\left. - \sum_{n=0}^{\infty} \left[A_{n-1} \sinh(n-\frac{1}{2}) \xi + B_{n-1} \cosh(n-\frac{1}{2}) \xi \right] \frac{n(n-1)}{(2n-1)} P_n(t) \right\} +$$

$$\sum_{n=0}^{\infty} 2\sqrt{2} U_1 e^{-(n+\frac{1}{2}) \xi} P_n(t) \quad (8b)$$

Cancelling the summations and P_n on both sides, expression (3.39) is obtained.

Equation (9) can be written as

$$\begin{aligned}
 & (\cosh \xi - t)^{\frac{1}{2}} \sin \eta \sum_{n=1}^{\infty} \left[C_n \cosh(n+\frac{1}{2})\xi + D_n \sinh(n+\frac{1}{2})\xi \right] P'_n(t) \\
 & = - \frac{2(\cosh \xi - t)}{\sinh \xi} (\cosh \xi - t)^{\frac{1}{2}} \sin \eta \sum_{n=1}^{\infty} \left[A_n \sinh(n+\frac{1}{2})\xi + B_n \cosh(n+\frac{1}{2})\xi \right] P'_n(t) \quad (9a)
 \end{aligned}$$

Using the following recurrence formulae

$$tP'_n(t) = \frac{n+1}{2n+1} P'_{n-1}(t) + \frac{n}{2n+1} P'_{n+1}(t)$$

equation (9a) can be written as

$$\begin{aligned}
 & \sum_{n=1}^{\infty} \left[C_n \cosh(n+\frac{1}{2})\xi + D_n \sinh(n+\frac{1}{2})\xi \right] P'_n(t) \\
 & = \frac{2}{\sinh \xi} \sum_{n=1}^{\infty} \left[A_{n+1} \sinh(n+\frac{3}{2})\xi + B_{n+1} \cosh(n+\frac{3}{2})\xi \right] \frac{n+2}{2n+3} P'_n(t) \\
 & - 2 \coth \xi \sum_{n=1}^{\infty} \left[A_n \sinh(n+\frac{1}{2})\xi + B_n \cosh(n+\frac{1}{2})\xi \right] P'_n(t) \\
 & + \frac{2}{\sinh \xi} \sum_{n=1}^{\infty} \left[A_{n-1} \sinh(n-\frac{1}{2})\xi + B_{n-1} \cosh(n-\frac{1}{2})\xi \right] \frac{n-1}{2n-1} P'_n(t) \quad (9b)
 \end{aligned}$$

Again, cancelling the summations on both sides of equation (9b) results in equation (3.38).

APPENDIX 7

The expressions for the coefficients of A_{n+1} , A_n , A_{n-1} , B_{n+1} , B_n , B_{n-1} , in the continuity equations (3.45) of Section 3.2.2.

These coefficients are as follows:

In equation (3.45.1)

$$\begin{aligned}
 A_{11} = & \left[\left(\frac{\beta_{01} q_{12}}{z_{02} \sinh \xi_2} - \frac{\beta_{02} q_{11}}{z_{01} \sinh \xi_1} \right) \frac{10}{(\beta_{01} - \beta_{02})} \frac{n+2}{2n+3} \right. \\
 & + \left(\frac{\coth \xi_1 q_{11} \beta_{12}}{z_{11}} - \frac{\coth \xi_2 q_{12} \beta_{11}}{z_{12}} \right) \frac{2(n+2)}{(\beta_{11} - \beta_{12})} \\
 & + \left(\frac{\beta_{01} q_{12}}{z_{02} \sinh \xi_2} - \frac{\beta_{02} q_{11}}{z_{01} \sinh \xi_1} \right) \frac{2(n+1)(n+2)}{(2n+3)(\beta_{01} - \beta_{02})} \\
 & \left. + \left(\frac{\beta_{01} q_{12}}{z_{02} \sinh \xi_2} - \frac{\beta_{02} q_{11}}{z_{01} \sinh \xi_1} \right) \frac{2(n-1)(n+2)}{(2n+3)(\beta_{01} - \beta_{02})} - 2(n+2) \right] \\
 \\
 A_{01} = & \left[\left(\frac{\coth \xi_1 q_{01} \beta_{02}}{z_{01}} - \frac{\coth \xi_2 q_{02} \beta_{01}}{z_{02}} \right) \frac{10}{(\beta_{01} - \beta_{02})} \right. \\
 & + \left(\frac{q_{01} \beta_{-12}}{\sinh \xi_1 z_{-11}} - \frac{q_{02} \beta_{-11}}{\sinh \xi_1 z_{-11}} \right) \frac{2}{(\beta_{-11} - \beta_{-12})} \frac{(n-1)(n+1)}{(2n+1)} \\
 & + \left(\frac{\beta_{11} q_{02}}{\sinh \xi_2 z_{12}} - \frac{\beta_{12} q_{01}}{\sinh \xi_1 z_{11}} \right) \frac{2n(n+2)}{(2n+1)} \frac{1}{(\beta_{11} - \beta_{12})} \\
 & + \left(\frac{\beta_{-12} q_{01}}{z_{-11} \sinh \xi_1} - \frac{\beta_{-11} q_{02}}{z_{-12} \sinh \xi_2} \right) \frac{n(n+1)}{(2n+1)} \frac{1}{(\beta_{-11} - \beta_{-12})} \\
 & + \left(\frac{\beta_{11} q_{02}}{z_{12} \sinh \xi_2} - \frac{\beta_{12} q_{01}}{z_{11} \sinh \xi_1} \right) \frac{n(n+1)}{(2n+1)} \frac{1}{(\beta_{11} - \beta_{12})} \\
 & + \left(\frac{\beta_{-12} q_{01}}{z_{-11} \sinh \xi_1} - \frac{\beta_{-11} q_{02}}{z_{-12} \sinh \xi_2} \right) \frac{(n-2)(n-1)}{(2n+1)} \frac{1}{(\beta_{-11} - \beta_{-12})} \\
 & \left. + \left(\frac{\beta_{11} q_{02}}{z_{12} \sinh \xi_2} - \frac{\beta_{12} q_{01}}{z_{11} \sinh \xi_1} \right) \frac{(n+2)(n+3)}{(2n+1)} \frac{1}{(\beta_{11} - \beta_{12})} + 2(2n+1) \right]
 \end{aligned}$$

$$\begin{aligned}
AA1 = & \left[\left(\frac{\beta_{01} q_{-12}}{\sinh \xi_2 z_{02}} - \frac{\beta_{02} q_{-11}}{\sinh \xi_1 z_{01}} \right) \frac{10 R_4}{R_8 \times BO} \right. \\
& + \left(\frac{\coth \xi_2 \beta_{-11} q_{-12}}{z_{-12}} - \frac{\coth \xi_1 \beta_{-12} q_{-11}}{z_{-11}} \right) \frac{2R_4}{BM} \\
& + \left(\frac{\beta_{02} q_{-11}}{z_{01} \sinh \xi_1} - \frac{\beta_{01} q_{-12}}{z_{02} \sinh \xi_2} \right) \frac{2nR_4}{R_8 \times BO} \\
& \left. + \left(\frac{\beta_{02} q_{-11}}{z_{01} \sinh \xi_1} - \frac{\beta_{01} q_{-12}}{z_{02} \sinh \xi_2} \right) \frac{2R_4 R_1}{R_8 \times BO} - 2R_4 \right]
\end{aligned}$$

$$\begin{aligned}
B11 = & \left[\left(\frac{z_{12} \beta_{01}}{\sinh \xi_2 z_{02}} - \frac{z_{11} \beta_{02}}{\sinh \xi_1 z_{01}} \right) \frac{10 R_1}{R_2 \times BO} \right. \\
& + (\coth \xi_1 \beta_{12} - \coth \xi_2 \beta_{11}) \frac{2 R_1}{BP} + \left(\frac{\beta_{01} z_{12}}{z_{02} \sinh \xi_2} - \frac{\beta_{02} z_{11}}{z_{01} \sinh \xi_1} \right) \\
& \left. \frac{2R_3 R_1}{R_2 \times BO} + \left(\frac{\beta_{01} z_{12}}{z_{02} \sinh \xi_2} - \frac{\beta_{02} z_{11}}{z_{01} \sinh \xi_1} \right) \frac{2R_4 R_1}{R_2 \times BO} \right]
\end{aligned}$$

$$\begin{aligned}
BO1 = & \left[(\coth \xi_1 \beta_{02} - \coth \xi_2 \beta_{01}) \frac{10}{BO} + \left(\frac{z_{01} z_{-12}}{\sinh \xi_1 z_{-11}} - \frac{z_{02} \beta_{-11}}{\sinh \xi_2 z_{-12}} \right) \right. \\
& \frac{2R_4 R_3}{R_4 \times BM} + \left(\frac{\beta_{11} z_{02}}{\sinh \xi_2 z_{12}} - \frac{\beta_{12} z_{01}}{\sinh \xi_1 z_{11}} \right) \frac{2n R_1}{R_5 \times BP} \\
& + \left(\frac{\beta_{-12} z_{01}}{\sinh \xi_1 z_{-11}} - \frac{\beta_{-11} z_{02}}{\sinh \xi_2 z_{-12}} \right) \frac{nR_3}{R_5 \times BM} \\
& + \left(\frac{\beta_{11} z_{02}}{\sinh \xi_2 z_{12}} - \frac{\beta_{12} z_{01}}{\sinh \xi_1 z_{11}} \right) \frac{nR_3}{R_5 \times BP} + \left(\frac{\beta_{-12} z_{01}}{z_{-11} \sinh \xi_1} - \frac{\beta_{-11} z_{02}}{\sinh \xi_2 z_{-12}} \right) \\
& \left. \frac{R_6 R_4}{R_5 \times BM} + \left(\frac{\beta_{11} z_{02}}{\sinh \xi_2 z_{12}} - \frac{\beta_{12} z_{01}}{z_{11} \sinh \xi_1} \right) \frac{R_1 R_7}{R_5 \times BP} \right]
\end{aligned}$$

$$\begin{aligned}
BB1 = & \left[\left(\frac{\beta_{01} z_{-12}}{\sinh \xi_2 z_{02}} - \frac{z_{-11} \beta_{02}}{\sinh \xi_1 z_{01}} \right) \frac{10 R_4}{R_8 \times BO} \right. \\
& + (\coth \xi_2 \beta_{-11} - \coth \xi_1 \beta_{-12}) \frac{2 R_4}{BM} \\
& + \left(\frac{\beta_{02} z_{-11}}{\sinh \xi_1 z_{01}} - \frac{\beta_{01} z_{-12}}{z_{02} \sinh \xi_2} \right) \frac{2n R_4}{R_8 \times BO} \\
& \left. + \left(\frac{\beta_{02} z_{-11}}{\sinh \xi_1 z_{01}} - \frac{\beta_{01} z_{-12}}{\sinh \xi_2 z_{02}} \right) \frac{2 R_4 R_1}{R_8 \times BO} \right]
\end{aligned}$$

$$\begin{aligned}
CONS1 = & \frac{4\sqrt{2}}{BO} \left(\frac{U_2 \beta_{01} e^{(n+\frac{1}{2})\xi_2}}{z_{02}} - \frac{U_1 \beta_{02} e^{-(n+\frac{1}{2})\xi_1}}{z_{01}} \right) \\
& + \frac{2\sqrt{2}}{BM} \left(\frac{-U_2 \beta_{-11} e^{(n-\frac{1}{2})\xi_2}}{z_{-12}} + \frac{U_1 \beta_{-12} e^{-(n-\frac{1}{2})\xi_1}}{z_{-11}} \right) \\
& + \frac{2\sqrt{2}}{BP} \left(\frac{-U_2 \beta_{11} e^{(n+\frac{3}{2})\xi_2}}{z_{12}} + \frac{U_1 \beta_{12} e^{-(n+\frac{3}{2})\xi_1}}{z_{11}} \right)
\end{aligned}$$

In equation (3.45.2)

$$\begin{aligned}
A22 = & \left[\left(\frac{q_{11}}{\sinh \xi_1 z_{01}} - \frac{q_{12}}{\sinh \xi_2 z_{02}} \right) \frac{10 R_1}{R_2 \times BO} \right. \\
& + \left(\frac{\coth \xi_2 q_{12}}{z_{12}} - \frac{\coth \xi_1 q_{11}}{z_{11}} \right) \frac{2 R_1}{BP} \\
& + \left(\frac{q_{11}}{z_{01} \sinh \xi_1} - \frac{q_{12}}{z_{02} \sinh \xi_2} \right) \frac{2R_3 R_1}{R_2 \times BO} \\
& \left. + \left(\frac{q_{11}}{z_{01} \sinh \xi_1} - \frac{q_{12}}{z_{02} \sinh \xi_2} \right) \frac{2R_4 R_1}{R_2 \times BO} \right]
\end{aligned}$$

$$\begin{aligned}
A02 = & \left[\left(\frac{\coth \xi_2 q_{02}}{z_{02}} - \frac{\coth \xi_1 q_{01}}{z_{01}} \right) \frac{10}{BO} \right. \\
& + \left(\frac{q_{02}}{\sinh \xi_2 z_{-12}} - \frac{q_{01}}{\sinh \xi_1 z_{-11}} \right) \frac{2 R_4 R_3}{R_5 \times BM} \\
& + \left(\frac{q_{01}}{\sinh \xi_1 z_{11}} - \frac{q_{02}}{\sinh \xi_2 z_{12}} \right) \frac{2n R_1}{R_5 \times BP} \\
& + \left(\frac{q_{02}}{\sinh \xi_2 z_{-12}} - \frac{q_{01}}{\sinh \xi_1 z_{-11}} \right) \frac{n R_3}{R_5 \times BM} \\
& + \left(\frac{q_{01}}{z_{11} \sinh \xi_1} - \frac{q_{02}}{\sinh \xi_2 z_{12}} \right) \frac{n R_3}{R_5 \times BP} \\
& + \left(\frac{q_{02}}{z_{-12} \sinh \xi_2} - \frac{q_{01}}{z_{-11} \sinh \xi_1} \right) \frac{R_4 R_6}{R_5 \times BM} \\
& \left. + \left(\frac{q_{01}}{z_{11} \sinh \xi_1} - \frac{q_{02}}{z_{12} \sinh \xi_2} \right) \frac{R_1 R_7}{R_5 \times BP} \right]
\end{aligned}$$

$$\begin{aligned}
AA2 = & \left[\left(\frac{q_{-11}}{\sinh \xi_1 z_{01}} - \frac{q_{-12}}{\sinh \xi_2 z_{02}} \right) \frac{10 R_4}{R_8 \times BO} \right. \\
& + \left(\frac{\coth \xi_1 q_{-11}}{z_{-11}} - \frac{\coth \xi_2 q_{-12}}{z_{-12}} \right) \frac{2 R_4}{BM} \\
& + \left(\frac{q_{-12}}{z_{02} \sinh \xi_2} - \frac{q_{-11}}{z_{01} \sinh \xi_1} \right) \frac{2n R_4}{R_8 \times BO} \\
& \left. + \left(\frac{q_{-12}}{z_{02} \sinh \xi_2} - \frac{q_{-11}}{z_{01} \sinh \xi_1} \right) \frac{2 R_4 R_1}{R_8 \times BO} \right]
\end{aligned}$$

$$\begin{aligned}
B22 &= \left[\left(\frac{z_{11}}{\sinh \xi_1 z_{01}} - \frac{z_{12}}{\sinh \xi_2 z_{02}} \right) \frac{10 R_1}{R_2 \times BO} \right. \\
&+ (\coth \xi_2 - \coth \xi_1) \frac{2 R_1}{BP} + \left. \left(\frac{z_{11}}{z_{01} \sinh \xi_1} - \frac{z_{12}}{z_{02} \sinh \xi_2} \right) \frac{2 R_3 R_1}{R_2 \times BO} \right. \\
&+ \left. \left(\frac{z_{11}}{z_{01} \sinh \xi_1} - \frac{z_{12}}{z_{02} \sinh \xi_2} \right) \frac{2 R_4 R_1}{R_2 \times BO} - 2R_1 \right] \\
\\
BO2 &= \left[(\coth \xi_2 - \coth \xi_1) \frac{10}{BO} + \left(\frac{z_{02}}{\sinh \xi_2 z_{-12}} - \frac{z_{01}}{\sinh \xi_1 z_{-11}} \right) \frac{2 R_4 R_3}{R_5 \times BM} \right. \\
&+ \left(\frac{z_{01}}{\sinh \xi_1 z_{11}} - \frac{z_{02}}{\sinh \xi_2 z_{12}} \right) \frac{2n R_1}{R_5 \times BP} \\
&+ \left(\frac{z_{02}}{z_{-12} \sinh \xi_2} - \frac{z_{01}}{z_{-11} \sinh \xi_1} \right) \frac{nR_3}{R_5 \times BM} \\
&+ \left(\frac{z_{01}}{z_{11} \sinh \xi_1} - \frac{z_{02}}{z_{12} \sinh \xi_2} \right) \frac{n R_3}{R_5 \times BP} \\
&+ \left(\frac{z_{01}}{z_{11} \sinh \xi_1} - \frac{z_{02}}{z_{12} \sinh \xi_2} \right) \frac{R_1 R_7}{R_5 \times BP} \\
&+ \left. \left(\frac{z_{02}}{z_{-12} \sinh \xi_2} - \frac{z_{01}}{z_{-11} \sinh \xi_1} \right) \frac{R_6 R_4}{R_5 \times BM} + 2R_5 \right] \\
\\
BB2 &= \left[\left(\frac{z_{-11}}{\sinh \xi_1 z_{01}} - \frac{z_{-12}}{\sinh \xi_2 z_{02}} \right) \frac{10 R_4}{R_8 \times BO} + (\coth \xi_1 - \coth \xi_2) \frac{2 R_4}{BM} \right. \\
&+ \left(\frac{z_{-12}}{z_{02} \sinh \xi_2} - \frac{z_{-11}}{z_{01} \sinh \xi_1} \right) \frac{2n R_4}{R_8 \times BO} \\
&+ \left. \left(\frac{z_{-12}}{z_{02} \sinh \xi_2} - \frac{z_{-11}}{z_{01} \sinh \xi_1} \right) \frac{2 R_4 R_1}{R_8 \times BO} - 2R_4 \right]
\end{aligned}$$

$$\begin{aligned}
\text{CONS2} = & \frac{4\sqrt{2}}{B0} \left(\begin{array}{cc} -(n+\frac{1}{2})\xi_1 & (n+\frac{1}{2})\xi_2 \\ \frac{U_1 e}{z_{01}} & - \frac{U_2 e}{z_{02}} \end{array} \right) + \frac{2\sqrt{2}}{BM} \left(\begin{array}{cc} -(n-\frac{1}{2})\xi_1 & (n-\frac{1}{2})\xi_2 \\ \frac{-U_1 e}{z_{-11}} & + \frac{U_2 e}{z_{-12}} \end{array} \right) \\
& + \frac{2\sqrt{2}}{BP} \left(\begin{array}{cc} -(n+\frac{3}{2})\xi_1 & (n+\frac{3}{2})\xi_2 \\ \frac{-U_1 e}{z_{11}} & + \frac{U_2 e}{z_{12}} \end{array} \right)
\end{aligned}$$

where

$$\begin{aligned}
q_{01} &= \sinh(n+\frac{1}{2})\xi_1 \\
q_{11} &= \sinh(n+\frac{3}{2})\xi_1 \\
q_{-11} &= \sinh(n-\frac{1}{2})\xi_1 \\
z_{02} &= \cosh(n+\frac{1}{2})\xi_2 \\
z_{12} &= \cosh(n+\frac{3}{2})\xi_2 \\
z_{-12} &= \cosh(n-\frac{1}{2})\xi_2 \\
\beta_0 &= \tanh(n+\frac{1}{2})\xi \\
\beta_1 &= \tanh(n+\frac{3}{2})\xi \\
\beta_{-1} &= \tanh(n-\frac{1}{2})\xi \\
B0 &= \beta_{01} - \beta_{02} \\
BP &= \beta_{11} - \beta_{12} \\
BM &= \beta_{-11} - \beta_{-12} \\
R_1 &= n+2 \\
R_2 &= 2n+3 \\
R_3 &= n+1 \\
R_4 &= n-1 \\
R_5 &= 2n+1 \\
R_6 &= n-2 \\
R_7 &= n+3 \\
R_8 &= 2n-1
\end{aligned}$$

APPENDIX 8Integration Procedure for Calculation of London/van der Waals
Potential between Two Spheres

The energy of interaction between two particles containing q_1 and q_2 atoms per cm^3 respectively is,

$$V_A = - \int_{V_1} q_1 dv_1 \int_{V_2} q_2 dv_2 \frac{\lambda_{12}}{r^6}$$

Consider a sphere of radius R_1 and an atom p outside this sphere so that $op = R$, Figure A8.1. The sphere R_1 cuts out from a second sphere of radius r around p a surface ABC which is

$$S_{ABC} = \int_0^{2\pi} d\phi \int_0^{\theta_0} d\theta r^2 \sin \theta$$

where

$$R_1^2 = R^2 + r^2 - 2rR \cos \theta_0$$

After integration,

$$S_{ABC} = \pi \frac{r}{R} [R_1^2 - (R-r)^2]$$

The volume of the hatched area in Figure A8.1 is

$$dv_1 = S_{ABC} \cdot dr$$

Therefore, the potential energy of an atom p may be written as

$$V_p = - \int_{R-R_1}^{R+R_1} \frac{\lambda_{12} q_1}{r^6} \pi \frac{r}{R} [R_1^2 - (R-r)^2] dr$$

With respect to a second sphere of radius R_2 , Figure A8.2, the centres being a distance C apart, the same procedure may be

APPENDIX 9Constants in the Expressions for Potential and Force of Attraction
(3.91) and (3.93) in Chapter 3

$$H_1 = \frac{A}{30}$$

$$H_2 = \frac{B}{60}$$

$$H_3 = \frac{AC}{15}$$

$$H_4 = \frac{AD}{60}$$

$$H_5 = \frac{BC}{60}$$

$$H_6 = \frac{BR_1}{60}$$

$$H_7 = \frac{Q}{210}$$

$$H_8 = \frac{BD}{180}$$

$$H_9 = \frac{CQ}{315}$$

$$H_{10} = \frac{QD}{420}$$

$$S_1 = -H_3 + H_1 \times R_1 - H_2$$

$$S_2 = -H_4 - H_3 \times R_1 + H_5 - \frac{5}{2} H_1 \times R_1^2 - H_6 + H_7$$

$$S_3 = H_8 + H_3 \times R_1^2 + 2H_5 \times R_1 - 2H_9 + H_1 \times R_1^3 \\ + \frac{7}{3} H_6 \times R_1 + 2H_7 \times R_1 - 2H_4 \times R_1$$

$$S_4 = -H_{10} - 2H_5 \times R_1^2 - 6H_9 \times R_1 - H_6 \times R_1^2 \\ - \frac{9}{2} H_7 \times R_1^2 + 3H_8 \times R_1$$

$$S_5 = 6H_9 \times R_1^2 + 2H_7 \times R_1^3 - 4H_{10} \times R_1$$

$$T_1 = H_3 + H_1 \times R_1 + H_2$$

$$T_2 = H_4 - H_3 \times R_1 - H_5 + \frac{5}{2} H_1 \times R_1^2 - H_6 - H_7$$

$$T_3 = -H_8 - H_3 \times R_1^2 + 2H_5 \times R_1 + 2H_9 + H_1 \times R_1^3 \\ - \frac{7}{3} H_6 \times R_1 + 2H_7 \times R_1 - 2H_4 \times R_1$$

$$T_4 = H_{10} + 2H_5 \times R_1^2 - 6H_9 \times R_1 - H_6 \times R_1^2 \\ + \frac{9}{2} H_7 \times R_1^2 + 3H_8 \times R_1$$

$$T_5 = -6H_9 \times R_1^2 + 2H_7 \times R_1^3 - 4H_{10} \times R_1$$

$$S_{11} = -2H_1$$

$$S_{22} = \frac{H_3}{2} - 2H_1 \times R_1 + H_2$$

$$S_{33} = -\frac{2}{3} H_5 + 2H_1 \times R_1^2 + 2H_6 - \frac{4}{3} H_7 + H_3 \times R_1$$

$$S_{44} = \frac{3}{2} H_9 - 2H_6 \times R_1 - 4H_7 \times R_1 - 2H_5 \times R_1$$

$$S_{55} = 6H_9 \times R_1 + 4H_7 \times R_1^2$$

$$T_{11} = 2H_1$$

$$T_{22} = -\frac{H_3}{2} - 2H_1 \times R_1 - H_2$$

$$T_{33} = \frac{2}{3} H_5 - 2H_1 \times R_1^2 + 2H_6 + \frac{4}{3} H_7 + H_3 \times R_1$$

$$T_{44} = -\frac{3}{2} H_9 + 2H_6 \times R_1 - 4H_7 \times R_1 - 2H_5 \times R_1$$

$$T_{55} = 6H_9 \times R_1 - 4H_7 \times R_1^2$$

APPENDIX 10Mathematical Procedure to obtain Equation (3.112) from (3.111)

Starting from equation (3.111) in Chapter 3, the right hand side can be processed as follows.

$$\frac{1}{(\cosh \xi - \cos \eta)^{3/2}} = \sum a_m P_n(\cos \eta)$$

Both sides can be multiplied by $P_m(\cos \eta)$ and integrated between $-1, 1$.

$$\int_{-1}^1 \frac{P_m(\cos \eta) d\mu}{(\cosh \xi - \cos \eta)^{3/2}} = \int_{-1}^1 \sum a_m P_m(\cos \eta) P_n(\cos \eta) d\mu = a_m \left(\frac{2}{2n+1} \right)$$

$$\int_{-1}^1 \frac{P_m(\cos \eta) d\mu}{(\cosh \xi - \mu)^{3/2}} = 2\sqrt{2} \frac{e^{-(n+\frac{1}{2})|\xi|}}{\sinh|\xi|}$$

$$a_m = (2n+1) \sqrt{2} \frac{e^{-(n+\frac{1}{2})|\xi|}}{\sinh|\xi|}$$

Therefore

$$\frac{1}{(\cosh \xi - \mu)^{3/2}} = \sum (2n+1) \sqrt{2} \frac{e^{-(n+\frac{1}{2})|\xi|}}{\sinh|\xi|} P_n(\cos \eta)$$

Replacing this relation in the R.H.S. of the equation (3.111) leads to

$$\text{R.H.S.} = \frac{1}{\sqrt{2}} c^2 v \sum \frac{e^{-(n+\frac{1}{2})|\xi|}}{\sinh|\xi|} (2n+1)(1-\mu^2) P_n(\mu)$$

Using the following recurrence relation,

$$(1-\mu^2) P_n(\mu) = \frac{(n+1)(n+2)}{(2n+1)(2n+3)} V_{n+1} - \frac{n(n-1)}{(2n+1)(2n-1)} V_{n-1}$$

The R.H.S. can be converted to

$$\begin{aligned} \text{R.H.S.} = & \frac{1}{\sqrt{2}} \frac{c^2 v}{\sinh|\xi|} \sum_{n=0}^{\infty} \frac{(n+1)(n+2)}{(2n+3)} e^{-(n+\frac{1}{2})|\xi|} V_{n+1} \\ & - \frac{n(n-1)}{(2n-1)} e^{-(n+\frac{1}{2})|\xi|} V_{n-1} \end{aligned}$$

V_{n-1} and V_{n+1} can be expressed in terms of V_n . By doing so and replacing the results in (3.111), equation (3.112) will be obtained.

$$\begin{aligned} \left[A_n \cosh(n+\frac{1}{2}) \xi + B_n \sinh(n+\frac{1}{2}) \xi \right] &= \frac{1}{\sqrt{2}} c^2 v \frac{1}{\sinh|\xi|} \frac{n(n+1)}{(2n+1)} \\ &\times \left[e^{-(n-\frac{1}{2})|\xi|} - e^{-(n+\frac{3}{2})|\xi|} \right] \end{aligned}$$

The expression of history integral as included in the equations of motion (3.117 - 3.120) is

Clift (1975) has solved this integral for fixed intervals of time by converting it into the two following integrals:

The first integral is calculated using Simpson rule or Simpson rule accompanied by trapezoidal rule depending on whether $N(N = \frac{t}{\Delta t})$ is even or odd. When N is even Simpson rule is used throughout the integration. When N is odd trapezoidal rule is used for the first integration step, Simpson rule being used for the rest. The second integral is solved assuming that U is a quadratic function of τ in the interval $(t-2\Delta t) < \tau < t$, i.e.

Therefore the history integral results in the two following expressions.

$$I_H = \sqrt{\Delta t} \left[\frac{4\sqrt{2}}{5} U_N^o + \frac{16\sqrt{2}}{15} U_{N-1}^o + \frac{3\sqrt{2}}{10} U_{N-2}^o + U_0^o \right]$$

$$+ \frac{4}{3} \sum_{i=1}^{N-3} \frac{\overset{\circ}{U}_i}{\sqrt{N-i}} + \frac{2}{3} \sum_{i=2}^{N-4} \frac{\overset{\circ}{U}_i}{\sqrt{N-i}} \quad (3)$$

For N odd

$$I_H = \sqrt{\Delta t} \left[\frac{4\sqrt{2}}{5} \overset{o}{U}_N + \frac{16\sqrt{2}}{15} \overset{o}{U}_{N-1} + \frac{3\sqrt{2}}{10} \overset{o}{U}_{N-2} + \frac{5}{6} \frac{\overset{o}{U}_1}{\sqrt{N-1}} + \frac{\overset{o}{U}_0}{2\sqrt{N}} \right. \\ \left. + \frac{4}{3} \sum_{\substack{i=2 \\ \text{(even)}}}^{N-3} \frac{\overset{o}{U}_i}{\sqrt{N-i}} + \frac{2}{3} \sum_{\substack{i=3 \\ \text{(odd)}}}^{N-4} \frac{\overset{o}{U}_i}{\sqrt{N-i}} \right] \quad (4)$$

or, in general,

$$(I_H)_N = S_N + B \overset{o}{U}_N \quad (5)$$

where S_N is only dependent on the past values of $\overset{o}{U}_N$ and B is independent of $\overset{o}{U}_N$.

In the present work, the integration step (H) is variable, therefore the above method had to be modified.

The total range of integral (0 → t) is divided into a number of equal intervals, HS (Figure A11.1). Initially, the value of history integral can be assumed to be zero, i.e. $S = 0$ and $B = 0$. In order to calculate the history integral at A (after one integration step), a straight line ($y = a\tau + b$) is fitted between 1 and A and, after carrying out the integration, the values of S and B are found to be

$$S = \frac{2}{3} \overset{o}{U}_1 \sqrt{t} \quad \text{for straight line}$$

$$B = \frac{4}{3} \sqrt{t}$$

This procedure is continued until one HS is completed ($I = 2$).

For the next interval, the information at 1, 2 is used to predict S and B at A_1 . For that a quadratic function ($y = a\tau^2 + b\tau + c$) is fitted through points 1, 2 and A_1 .

From then on, Clift's procedure is followed with the exception that the parabola is always fitted through the last three non-

equidistant points.

A summary of the procedure to calculate the integral for the rest of the interval is given in Table All.1.

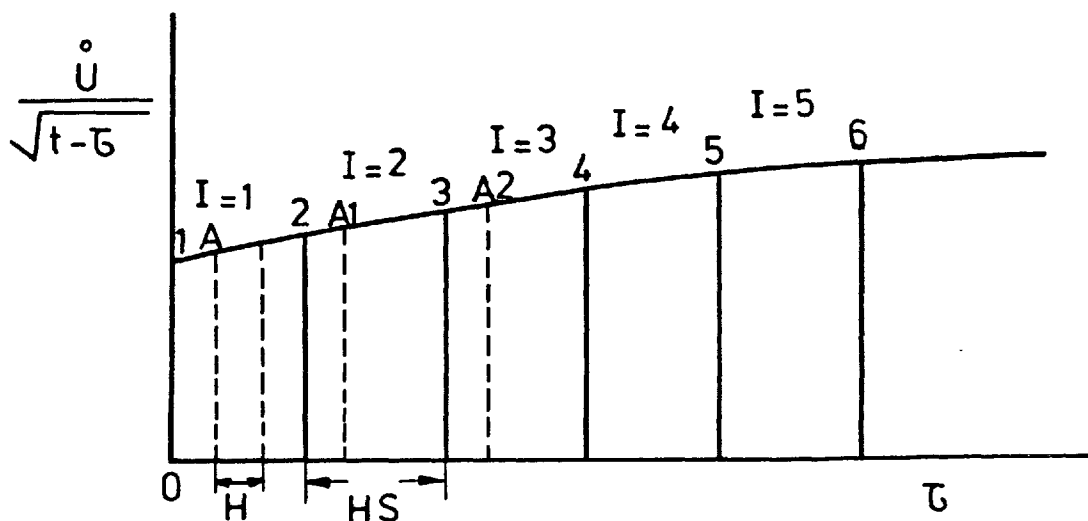
Information at points 1, 2, 3, 4, ... is always kept in the computer memory and used to predict the history integral at the next point.

TABLE All.1 Method used to calculate the history integral

$I = 1$	straight line
$I = 2$	parabola
$I = 3$	trapezoidal rule + parabola
$I = 4$	Simpson rule + parabola
$I > 4, I \text{ odd}$	trapezoidal rule + Simpson rule + parabola
$I > 4, I \text{ even}$	Simpson rule + parabola

A subroutine (SUBROUTINE BASS) was written in order to calculate S and B at any time.

FIGURE All.1: Procedure for calculation of the history integral



COMPUTER PROGRAMS

```

PROGRAM BUBBLE(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT,TAPE21)
DIMENSION Q(150),ID1(445),ID2(445),SAV(150),VAV(150)
DO 1 I=1,150
  SAV(I)=0.
  VAV(I)=0.
  1 Q(I)=0.
  READ,NB
  READ,C
  J=148
  W=5.
  AL=10.
  MM=NB+1
  M=1
  N=0
  D3=0.
  D4=0.
  AS=0.
  GS=0.
  ST=0.
  VT=0.
  GSM=0.
  GVM=0.
  SSD1=0.
  SVD1=0.
  READ(21,111) ((ID1(I),ID2(I)),I=1,NB)
  111 FORMAT(I5,1X,I5)
  100 D=(ID2(M)-ID1(M))*C
  IF(D,LE,0.) GO TO 200
  I=((D-AL)/W)+1
  IF((D,LT,AL).OR.(I,GT,J)) GO TO 200
  N=N+1
  D3=D3+D
  D4=D4+ALOG(D)
  Q(I)=Q(I)+1
  M=M+1
  IF(M,EQ,MM) GO TO 300
  GO TO 100
  200 PRINT,D
  M=M+1
  IF(M,EQ,MM) GO TO 300
  GO TO 100
  300 AMD=D3/N
  DO 332 I=1,J
    DPH=(Q(I)/N)*100.
    Y=DPH/W
    X=(I-0.5)*W+AL
    PRINT,X,Y
  332 CONTINUE
  DO 2 I=1,J
    AS=AS+Q(I)*(((I-0.5)*W+AL)-AMD)**2
  2 CONTINUE
  ASD=SQRT(AS/N)
  GMD=EXP(D4/N)
  DO 3 I=1,J
    GS=GS+Q(I)*((ALOG(SQRT(((I-1)*W+AL)*(I*W+AL)))-(D4/N))**2)
    SAV(I)=((I-1)*W+AL)*(I*W+AL)*Q(I)
    VAV(I)=((SQRT(((I-1)*W+AL)*(I*W+AL)))*3)*Q(I)
    ST=ST+SAV(I)
    VT=VT+VAV(I)
  3 CONTINUE
  GSD=EXP(SQRT(GS/N))
  DNS=SQRT(ST/N)
  DNV=(VT/N)**0.333333
  DO 12 I=1,J
    GSM=GSM+(ALOG(SQRT(((I-1)*W+AL)*(I*W+AL)))*(SAV(I)/ST)
  12 GVM=GVM+(ALOG(SQRT(((I-1)*W+AL)*(I*W+AL)))*(VAV(I)/VT)
    GSMD=EXP(GSM)
    GVMD=EXP(GVM)
    GSMD1=EXP(ALOG(GMD)+2.*(ALOG(GSD))**2)
    GVMD1=EXP(ALOG(GMD)+3.*(ALOG(GSD))**2)
  DO 14 I=1,J
    SSD1=SSD1+((ALOG(SQRT(((I-1)*W+AL)*(I*W+AL)))-GSM)**2)*(SAV(I)/ST)
    SVD1=SVD1+((ALOG(SQRT(((I-1)*W+AL)*(I*W+AL)))-GVM)**2)*(VAV(I)/VT)
  14 CONTINUE
  SSD=EXP(SQRT(SSD1))
  SVD=EXP(SQRT(SVD1))
  WRITE(6,101) N
  101 FORMAT(1H0,15X,"NO. OF BUBBLES :",5X,"N=",I5)
  WRITE(6,102)
  102 FORMAT(1H0,15X,"ARITHMETIC MEAN DIA.",10X,
+ "GEOMETRIC MEAN DIA.",10X,"GEO. SUR. MEAN DIA.",10X,
+ "GEO. VOL. MEAN DIA.",10X)
  WRITE(6,202) AMD,GMD,GSMD,GVMD
  202 FORMAT(12X,E17.8,14X,E17.8,13X,E17.8,14X,E17.8)
  WRITE(6,103)
  103 FORMAT(1H0,15X,"ARITHMETIC S. DIV.",12X,"GEOMETRIC S. DIV.",
+ 13X,"GEO. SUR. S. DIV.",13X,"GEO. VOL. S. DIV.",10X)
  WRITE(6,203) ASD,GSD,SSD,SVD
  203 FORMAT(12X,E17.8,3(14X,E17.8))
  WRITE(6,404) GSMD1,GVMD1,DNS,DNV
  404 FORMAT(12X,E17.8)
  STOP
  ENCL

```

1. PROGRAM BUBBLE

This program calculates different mean sizes for a bubble size distribution.

```

PROGRAM COULTER(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
  DIMENSION TAB(4,2),COR(2,2),G(3),X(4),Y(4),CP(2),CONS(9),AK(9),T(4
+) ,TL(14),AI(14),AM(14),RBL(14,2),C(14,8),RCC(14,4),BL(14),RC(14,4)
+,CC(14,4),E(14,4),DLV(14),DIFC(14,4),ADLV(14),CUR(9,4),ADLV1(9),
+ FREN(14,4),FCUM(14,4),V(14),VDIF(14,4),VDIFT(14,4),FREV(14,4),D(4)
+,D1(4),DGN(4),DGV(4),SIG(4),SIG1(4),SIGMA1(4),SIGMA2(4),FCUMV(14
+,4),DGV1(4),ERROR(9)
  READ,M,N
  READ,(T(I),I=1,M)
  READ,((TL(I),AI(I),AM(I)),I=1,N)
  M1=2*M
  READ,((C(I,J),J=1,M1),I=1,N)
  READ,((RBL(I,J),J=1,2),I=1,N)
  PI=4.*ATAN(1.)
  P=3.125
  CALF=1.0724
  SUMY=0.
  SUMY=0.
  SUMX=0.
  SUMX=0.
  SUMXY=0.
  DO 333 I=1,N
  DO 444 J=1,M
    RCC(I,J)=0.
    RC(I,J)=0.
    CC(I,J)=0.
    E(1,J)=0.
    DIFC(I,J)=0.
    FREN(I,J)=0.
    FCUM(I,J)=0.
    FREV(I,J)=0.
    FCUMV(I,J)=0.
    VDIF(I,J)=0.
    VDIFT(I,J)=0.
  444 CONTINUE
    BL(I)=0.
    DLV(I)=0.
    ADLV(I)=0.
  333 V(I)=0.
  DO 123 I=1,9
    ERROR(I)=0.
    CONS(I)=0.
    AK(I)=0.
    ADLV1(I)=0.
  DO 133 J=1,4
    133 CUR(I,J)=0.
  123 CONTINUE
  DO 666 I=1,4
    X(I)=0.
    666 Y(I)=0.
    K=1
  DO 5 I=1,N
    DO 6 J=1,M1,2
      RCC(I,K)=C(I,J)+C(I,J+1)
      6 K=K+1
      BL(I)=(RBL(I,1)+RBL(I,2))/2.
    DO 26 L=1,M
      RC(I,L)=RCC(I,L)/2.
      CC(I,L)=P*(RC(I,L)/1000.)**2
      26 E(I,L)=RC(I,L)+CC(I,L)-BL(I)
      DLV(I)=CALF*(TL(I)*AI(I)*AM(I))**0.333333
      K=1
    5 CONTINUE
    IL=1
    DO 4 I=1,N-1
      DO 17 L=1,M
        DIFC(I,L)=E(I+1,L)-E(I,L)
        IF(DIFC(I,L).LT.0.) DIFC(I,L)=0.
        ADLV(I)=(DLV(I+1)+DLV(I))/2.
        IF(ADLV(I).GT.4.2) GO TO 555
        CUR(IL,L)=ALOG(DIFC(I,1)/DIFC(I,L))
        ADLV1(IL)=ADLV(I)
      555 FREN(I,L)=(DIFC(I,L)/E(N,L))*100.
        IF(I.EQ.1) FCUM(I,L)=FREN(I,L)
        IF(I.NE.1) FCUM(I,L)=FCUM(I-1,L)+FREN(I,L)
        V(1)=PI*ADLV(I)**3/6.
        VDIF(I,L)=DIFC(1,L)*V(I)
        IF(I.EQ.1) VDIFT(I,L)=VDIF(I,L)
        17 IF(I.NE.1) VDIFT(I,L)=VDIFT(I-1,L)+VDIF(I,L)
        IF(ADLV(I).LT.4.2) IL=IL+1
      4 CONTINUE
    DO 7 I=1,N-1
      DO 77 L=1,M
        FREV(I,L)=(VDIF(I,L)/VDIFT(N-1,L))*100.
        77 FCUMV(I,L)=(VDIFT(I,L)/VDIFT(N-1,L))*100.
      7 CONTINUE
    DO 222 I=1,M
      D(I)=0.
      DGN(I)=0.
      D1(I)=0.
      DGV(I)=0.
      SIG(I)=0.

```

2. PROGRAM COULTER

This program calculates the flotation rate constant for individual particle sizes as well as the average rate constant and mean size of the particles.

```

SIGMA1(I)=0.
SIG1(I)=0.
SIGMA2(I)=0.
DGV1(I)=0.
ERROR(I)=0.
222 CCONTINUE
DO 19 L=1,M
DO 9 I=1,N-1
D(L)=C(L)+FREN(I,L)*ALOG(ADLV(I))
9 D1(L)=D1(L)+FREV(I,L)*ALOG(ADLV(I))
DGN(L)=EXP(D(L)/100.)
DGV(L)=EXP(D1(L)/100.)
DO 11 J=1,N-1
SIG(L)=SIG(L)+FREN(J,L)*(ALOG(ADLV(J))-ALOG(DGN(L)))*2
11 SIG1(L)=SIG1(L)+FREV(J,L)*(ALOG(ADLV(J))-ALOG(DGV(L)))*2
SIGMA1(L)=EXP((SIG(L)/100.)*0.5)
19 SIGMA2(L)=EXP((SIG1(L)/100.)*0.5)
DO 16 I=1,M
16 DGV1(I)=EXP(ALOG(DGN(I))+3.*(ALOG(SIGMA1(I)))*2)
DO 10 L=1,M
10 CUR(IL,L)=ALOG(VDIFT(N-1,1)/VDIFT(N-1,L))
DO 40 I=1,IL
K=1
IN=4
DO 30 J=1,IN
X(J)=T(J)
30 Y(J)=CUR(I,J)
J1=2
CALL POLYA(X,Y,IN,XSCALE,XSHIFT,K,J1,TAB,COR,G)
SHIFT1=0.
SCALE=1.
CALL POLYB(CP,SHIFT1,SCALE,IN,XSCALE,XSHIFT,K,J1,TAB,COR,G)
CONS(I)=CP(1)
AK(I)=CP(2)
DO 122 L=1,M
SUMYY=SUMYY+Y(L)**2
SUMY=SUMY+Y(L)
SUMXY=SUMXY+X(L)*Y(L)
SUMXX=SUMXX+X(L)**2
122 SUMX=SUMX+X(L)
VAR=(SUMYY-CONS(I)*SUMY-AK(I)*SUMXY)/(M-2)
ERROR(I)=SQRT(ABS(VAR))/SQRT(ABS(SUMXX-(SUMX**2)/M))
PRINT,SUMX,SUMY,SUMXX,SUMYY,SUMXY,VAR
SUMX=0.
SUMY=0.
SUMXX=0.
SUMYY=0.
SUMXY=0.
40 CONTINUE
WRITE(6,100)
100 FORMAT(1H0,/,1X,"DIA. AVERAGE",12X,"NO. FREQ.",17X,
+ "CUM. NO. FREQ.",16X,"VOL. FREQ.",16X,"CUM. VOL. FREQ.")
WRITE(6,200)
200 FORMAT(1H,/,1X,"(MICROMETER)",10X,"(PERCENTAGE)",14X,
+ "(PER. OVER SIZE)",12X,"(PERCENTAGE)",12X,"(PER. OVER SIZE)",///)
DO 1000 I=1,N-1
1000 WRITE(6,300) ADLV(I),(FREN(I,J),J=1,M),(FCUM(I,J),J=1,M),
+ (FREV(I,J),J=1,M),(FCUMV(I,J),J=1,M)
300 FORMAT( 3X,F5.2,5X,16(F5.1,2X))
WRITE(6,501)
501 FORMAT(1H0,/,24X,"GEOMETRIC MEAN DIAS. BY NO.",16X,
+ "STANDARD DIVIATIONS",/)
WRITE(6,502) ((DGN(I),SIGMA1(I)),I=1,4)
502 FORMAT( 15X,4(F5.2,5X),5X,4(F6.4,5X))
WRITE(6,601)
601 FORMAT(1H0,/,24X,"GEOMETRIC MEAN DIAS. BY VOL.",16X,
+ "STANDARD DIVIATIONS",/)
WRITE(6,602) ((DGV(I),SIGMA2(I)),I=1,4)
WRITE(6,602) (DGV1(I),I=1,4)
602 FORMAT( 15X,4(F5.2,5X),5X,4(F6.4,5X))
WRITE(6,201)
201 FORMAT(1H1,/,30X,"DIAMETER,MICRON",/)
WRITE(6,301) (ADLV1(I),I=1,IL-1),DGV(1)
301 FORMAT( 5X,6(1X,E10.3))
WRITE(6,202)
202 FORMAT(1H,/,35X,"CURVE POINTS",/)
WRITE(6,203)
203 FORMAT( 32X,"Y",35X,"X",/)
WRITE(6,302) ((CUR(I,J),I=1,IL),X(J)),J=1,M)
302 FORMAT( 6(1X,E10.3),10X,F5.2)
WRITE(6,204)
204 FORMAT(1H,/,32X,"RATE CONSTANTS",/)
WRITE(6,303) (AK(I),I=1,IL)
303 FORMAT( 5X,6(1X,E10.3))
WRITE(6,205)
205 FORMAT(1H,/,34X,"CONSTANTS",/)
WRITE(6,304) (CONS(I),I=1,IL)
304 FORMAT( 5X,6(1X,E10.3))
WRITE(6,206)
206 FORMAT(1H,/,36X,"ERRORS",/)
WRITE(6,305) (ERROR(I),I=1,IL)
305 FORMAT( 5X,6(1X,E10.3))
STOP
END

```

3. PROGRAM TRAJ1

Determination of the trajectory of a particle as it approaches a bubble from a far distance to a distance of separation of 4 bubble radii between their centres.

```

PROGRAM TRAJ1(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT,TAPE13)
C
C THIS PROGRAM CALCULATES THE INITIAL POINTS FOR INTEGRATION AND
C DETERMINES THE TRAJECTORY OF A PARTICLE APPROACHING A BUBBLE
C USING HABER'S APPROXIMATE SOLUTION FOR CORRECTION FACTORS;
C MODIFIED EULER METHOD IS USED FOR INTEGRATION.
C
COMMON/T/ YA(6),YG(6),YM1(6),YPM1(6),YO(6),YPO(6),YM1A(6)
+,YPP1(6),YP1(6),YH(6),YYP(6),YH1(6),SSD,DIS,YPPP(6),CORK(6)
+,Y(4,6),F(4,6),COKR1(6)
COMMON/T4/UA1,UA2,UP1,UP2,ALAM1A,ALAM2A,ALAM1P,ALAM2P
COMMON/T5/RA,PI,DEF,DE1,DE2,R1,R2,AMU,ANU,G1,G2,FPB,FB,RE1,UB,H2
COMMON/T3/X,HS,IKLAG,IND1,UD(400,4),S(4),B(4)
READ,ERROR,H
KONT=0
DIS=0.08
R1=50.E-04
R2=10.E-04
RA=R2/R1
DEF=1.
DE1=0.0012
DE2=2.5
AMU=0.01
ANU=AMU/DEF
GR=981.8
PI=4.*ATAN(1.)
UB=2.*R1**2*(DEF-DE1)*GR/(9.*AMU)
FB=6.*PI*AMU*R1*UB
G1=SQRT(R1*UB)/SQRT(PI*ANU)
G2=R2*SQRT(UB)/SQRT(R1*PI*ANU)
H2=RA**2*(DEF-DE2)/(DEF-DE1)
GF=2.*(DE2-DEF)*R2**2*GR/(9.*AMU*UB)
AKF=2.*DE2*H2**2*UB/(9.*AMU*R1)
FPB=FB*RA
RE1=R1*UB*DE1/AMU
IND1=1
HS=0.08
X=0.
IKLAG=1
C
C CALCULATION OF STARTING POINTS FOR INTEGRATION
C
YO(5)=50.
YO(6)=0.5
YOO=SQRT(YO(5)**2+YO(6)**2)
SITET=YO(6)/YOO
COTET=YO(5)/YOO
ALP=1./YOO
BET=RA/YOO
AKAZ=1.+9.*ALP*BET/4.+9.*BET**3*ALP/4.-9.*ALP**3*BET/2.+81.*ALP
**2*BET**2/16.
AKBZ=-3.*BET/2.+BET**3/2.+BET*ALP**2/2.-27.*BET**2*ALP/8.
AKAX=1.+9.*ALP*BET/16.+9.*BET**3*ALP/8.+3.*ALP**3*BET/8.+81.
**ALP**2*BET**2/256.
AKBX=-(3.*BET/4.+BET**3/4.+BET*ALP**2/4.+27.*BET**2*ALP/64.+
+63.*ALP*BET**4/64.+63.*ALP**3*BET**2/64.+243.*ALP**2*BET**
+3/1024.)
ALBZ=1.+9.*ALP*BET/4.+9.*ALP**3*BET/4.-9.*BET**3*ALP/2.+81.*
+ALP**2*BET**2/16.
ALAZ=-3.*ALP/2.+ALP**3/2.+ALP*BET**2/2.-27.*ALP**2*BET/8.
ALBX=1.+9.*ALP*BET/16.+9.*ALP**3*BET/8.+3.*BET**3*ALP/8.+81.
**ALP**2*BET**2/256.
ALAX=-(3.*ALP/4.+ALP**3/4.+ALP*BET**2/4.+27.*ALP**2*BET/64.+63.*BE
+T*ALP**4/64.+63.*BET**3*ALP**2/64.+243.*BET**2*ALP**3/1024.)
DET1=AKAZ*ALBZ-AKBZ*ALAZ
DET2=AKAX*ALBX-AKBX*ALAX
UAZ=(COTET*ALBZ-H2*COTET*AKBZ)/DET1
UBZ=(COTET-AKAZ*UAZ)/AKBZ
UAX=(SITET*ALBX-H2*SITET*AKBX)/DET2
UBX=(SITET-AKAX*UAX)/AKBX
YO(1)=UAZ*COTET+UAX*SITET
YO(2)=UBZ*COTET+UBX*SITET
YO(3)=UAZ*SITET-UAX*COTET
YO(4)=-UBX*COTET+UBZ*SITET
DO 2 I=1,6
2 YA(I)=YO(I)
CALL DERV
GO TO 3001
DO 29 I=1,4
29 UD(1,I)=YG(I)
3001 CONTINUE
DO 3 I=1,6
3 YPO(I)=YG(I)

```

```

120 DO 4 I=1,6
    YM1(I)=YA(I)-H*YPO(I)
    4 YA(I)=YM1(I)
14 CALL DERV
24 DO 5 I=1,6
    5 YPM1(I)=YG(I)
    DO 7 I=1,6
    7 YM1A(I)=YO(I)-(H/2.)*(YPO(I)+YPM1(I))
    DO 8 I=1,6
    8 YH1(I)=ABS((YM1A(I)-YM1(I))/YM1A(I))
    DO 175 I=1,6
    IF(YH1(I).GT.ERROR) GO TO 198
175 CONTINUE
    GO TO 64
198 DO 60 I=1,6
    60 YA(I)=YM1A(I)
    DO 99 I=1,6
    99 YM1(I)=YM1A(I)
    GO TO 14
64 PRINT,(YM1A(I),I=1,6)

C
C      INTEGRATION STARTS
C
    DO 11 I=1,6
    YM1(I)=YM1A(I)
    YP1(I)=YM1(I)+2.*H*YPO(I)
    YPPP(I)=YP1(I)
11 YA(I)=YP1(I)
50 X=X+H
40 CALL DERV
    DO 19 I=1,6
    YPP1(I)=YG(I)
    YP1(I)=YO(I)+(H/2.)*(YPO(I)+YPP1(I))
    YP1(I)=YP1(I)+(1./5.)*(YPPP(I)-YP1(I))
19 YH(I)=(YA(I)-YP1(I))/YP1(I)
    DO 20 I=1,6
    IF(ABS(YH(I)).GT.ERROR) GO TO 66
20 CONTINUE
    DO 187 I=1,6
187 CORR(I)=(YPPP(I)-YP1(I))
    GO TO 65
66 INDI=2
    DO 30 I=1,6
    30 YA(I)=YP1(I)
    GO TO 40
65 CONTINUE
    DO 70 I=1,6
    70 YA(I)=YP1(I)
    INDI=3
    DIS=HS*IKLAG
    IF((ABS(X-DIS).GT.1.E-6)) GO TO 199
    IKLAG=IKLAG+1
    WRITE(6,1802) IKLAG,X
1802 FORMAT(1X,I6,E17,8)
    WRITE(6,1801) (YP1(I),I=1,6)
    WRITE(6,1801) ALAM1A,ALAM2A,ALAM1P,ALAM2P,UA1,UA2,UP1,UP2
1801 FORMAT(1X,8E14,6)
199 CALL DERV
    IF(YP1(5).GT.4.) GO TO 797
    KONT=KONT+1
    DO 898 I=1,6
    Y(KONT,I)=YP1(I)
898 F(KONT,I)=YG(I)
    IF(KONT.EQ.4) GO TO 33
797 DO 80 I=1,6
    YPO(I)=YG(I)
    YM1(I)=YO(I)
    YO(I)=YP1(I)
    YP1(I)=YM1(I)+2.*H*YPO(I)
    YPPP(I)=YP1(I)
    YYP(I)=YP1(I)-(4./5.)*CORR(I)
80 YA(I)=YYP(I)
    INDI=1
    X=X+H
    GO TO 40
33 DO 83 I=1,6
83 CORR1(I)=-CORR(I)
    WRITE(13,1999) IKLAG,X,H
1999 FORMAT(16,2E17,8)
    WRITE(13,2000) ((Y(J,I),I=1,6),(F(J,I),I=1,6)),J=1,4
    WRITE(13,2000) (CORR1(I),I=1,6)
2000 FORMAT(6E17,8)
716 STOP
    END

SUBROUTINE DERV
C
C      THIS SUBROUTINE CALCULATES THE DERIVATIVES
C      IN THE EQUATIONS OF MOTION.
C
    COMMON/T/YA(6),YG(6),YM1(6),YPM1(6),YO(6),YPO(6),YM1A(6)
    +,YPP1(6),YP1(6),YH(6),YYP(6),YH1(6),SSD,DIS,YPPP(6),CORR(6)

```

```

*)Y(4,6)*F(4,6)*CORR1(6)
COMMON/T4/UA1,UA2,UP1,UP2,ALAM1A,ALAM2A,ALAM1P,ALAM2P
COMMON/T3/X,HS,IKLAG,IND1,UD(400,4),S(4),B(4)
COMMON/T5/RA,P1,DEF,DE1,DE2,R1,R2,AMU,ANU,G1,G2,FPB,FB,HE1,UB,H2
CCD=SQRT(YA(5)**2+YA(6)**2)
SSU=CCD-(1.+RA)
SS=SSC*R1
UP1=(YA(1)*YA(6)-YA(3)*YA(5))/CCD
UP2=(YA(2)*YA(6)-YA(4)*YA(5))/CCD
UA1=(YA(1)*YA(5)+YA(3)*YA(6))/CCD
UA2=(YA(2)*YA(5)+YA(4)*YA(6))/CCD
ALP=R1/(CCD*R1)
BET=R2/(CCD*R1)
PRINT,CCD,ALP,BET
ALAM1A=(1.+9.*ALP*BET/4.+9.*BET**3*ALP/4.-9.*ALP**3*BET/2.
+81.*ALP**2*BET**2/16.)+(UA2/UA1)*(-3.*BET/2.+BET**3/2.+BET
+ALP**2/2.-27.*BET**2*ALP/8.)
ALAM2A=(1.+9.*ALP*BET/4.+9.*ALP**3*BET/4.-9.*BET**3*ALP/2.+81.*AL
P**2*BET**2/16.)+(UA1/UA2)*(-3.*ALP/2.+ALP**3/2.+ALP*BET**
+2/2.-27.*ALP**2*BET/8.)
ALAM1P=(1.+9.*ALP*BET/16.+9.*BET**3*ALP/8.+3.*ALP**3*BET/8.+81.*
ALP**2*BET**2/256.)-(UP2/UP1)*(3.*BET/4.+BET**3/4.+BET*ALP
**2/4.+27.*BET**2*ALP/64.+63.*ALP*BET**4/64.+63.*A
LP**3*BET**2/64.+243.*ALP**2*BET**3/1024.)
ALAM2P=(1.+9.*ALP*BET/16.+9.*ALP**3*BET/8.+3.*BET**3*ALP/8.+
+81.*ALP**2*BET**2/256.)-(UP1/UP2)*(3.*ALP/4.+ALP**3/4.+ALP
*BET**2/4.+27.*ALP**2*BET/64.+63.*BET*ALP**4/64.+63.*BET**
+3*ALP**2/64.+243.*BET**2*ALP**3/1024.)
FMOL=0.
E1=2.*RE1*(1.+0.5*(DEF/DE1))/9.
E2=2.*R2**2*UB*DE2*(1.+0.5*(DEF/DE2))/(9.*R1*AMU)
GO TO 3003
IF(IND1.GT.1) GO TO 202
CALL BASS
202 CONTINUE
3003 DO 3004 I=1,4
S(I)=0.
B(I)=0.
3004 CONTINUE
YG(1)=(1.-(UA1*ALAM1A*YA(5)/CCD+UP1*ALAM1P*YA(6)/CCD)-G1*S(1)+FMOL
+YA(5)/(FPB*CCD))/(E1+B(1)*G1)
YG(2)=(H2-(UA2*ALAM2A*YA(5)/CCD+UP2*ALAM2P*YA(6)/CCD)-G2*S(2)-FMOL
+YA(5)/(FPB*CCD))/(E2+B(2)*G2)
YG(3)=(UP1*ALAM1P*YA(5)/CCD-UA1*ALAM1A*YA(6)/CCD)-G1*S(3)+FMOL*
YA(6)/(FB*CCD))/(E1+B(3)*G1)
YG(4)=(UP2*ALAM2P*YA(5)/CCD-UA2*ALAM2A*YA(6)/CCD)-G2*S(4)-FMOL
+YA(6)/(FPB*CCD))/(E2+B(4)*G2)
YG(5)=YA(2)-YA(1)
YG(6)=YA(4)-YA(3)
IF(X.LE.0.) GO TO 27
IF(ABS(X-DIS).GT.1.E-6) GO TO 27
IF(IND1.LE.2) GO TO 27
GO TO 3002
990 DO 29 I=1,4
29 UD(IKLAG,I)=YG(I)
3002 CONTINUE
WRITE(6,1803) (YG(I),I=1,6)
1803 FORMAT(1X,6E17.8)
27 RETURN
END

SUBROUTINE BASS
C
C THIS SUBROUTINE CALCULATES S,S AND B,S REQUIRED
C FOR CALCULATION OF THE HISTORY INTEGRAL.
C
COMMON/T3/X,HS,IKLAG,IND1,UD(400,4),S(4),B(4)
IF(X.GT.0.) GO TO 180
DO 118 I=1,4
S(I)=0.
118 B(I)=0.
RETURN
180 IF(IKLAG.GT.1) GO TO 1
DO 107 I=1,4
S(I)=(2./3.)*UD(1,I)*SQRT(X)
107 B(I)=(4./3.)*SQRT(X)
RETURN
1 IF(IKLAG.GT.2) GO TO 2
D1=HS
D2=X-HS
DO 33 I=1,4
X1=0.
X2=D1
PE1=UD(1,I)
PE2=UD(2,I)
CALL AUX(D1,D2,PE1,PE2,X1,X2,X,SY,BX)
S(I)=SX
33 B(I)=BX

```

```

RETURN
2 IF (IKLAG.GT.3) GO TO 3
X1=HS
X2=2.*HS
D3=HS
D1=HS
D2=X-(D1+D3)
X3=X
DO 998 I=1,4
ZN=(UC(1,I)/SQRT(X)+UD(2,I)/SQRT(X-D3))*D3/2.
PE1=UC(2,I)
PE2=UC(3,I)
CALL AUX(D1,D2,PE1,PE2,X1,X2,X,SX,BX)
S(I)=ZN+SX
998 B(I)=BX
RETURN
3 IKLAG1=IKLAG/2
IKL=IKLAG-1
IKL1=IKLAG-2
AIKL=IKL
AIKL1=IKL1
IF (IKLAG1*2.NE.IKLAG) GO TO 4
DO 401 J=1,4
SUM=0.
DO 79 I=2,IKL,2
AI=I-1
79 SUM=SUM+(UD(I,J)/SQRT(X-AI*HS))*(4.*HS/3.)
IF (IKLAG.EQ.4) GO TO 401
DO 80 I=3,IKL1,2
AI=I-1
80 SUM=SUM+(UD(I,J)/SQRT(X-AI*HS))*(2.*HS/3.)
401 S(J)=SUM+(UD(1,J)/SQRT(X)+UD(IKL,J)/SQRT(X-(AIKL1*HS)))*HS/3.
GO TO 411
4 DO 133 I=1,4
133 S(I)=(UD(1,I)/SQRT(X)+UD(2,I)/SQRT(X-HS))*HS/2.
DO 406 J=1,4
SUM=0.
DO 89 I=3,IKL,2
AI=I-1
89 SUM=SUM+(UD(I,J)/SQRT(X-AI*HS))*(4.*HS/3.)
IF (IKLAG.EQ.5) GO TO 406
DO 100 I=4,IKL1,2
AI=I-1
100 SUM=SUM+(UD(I,J)/SQRT(X-AI*HS))*(2.*HS/3.)
406 S(J)=S(J)+(UD(2,J)/SQRT(X-HS)+UD(IKL,J)/SQRT(X-(AIKL1*HS)))*HS
+/3.+SUM
411 AIKLAG=IKLAG
D1=HS
D2=X-AIKL*HS
X1=AIKL1*HS
X2=X1+D1
DO 402 I=1,4
PE1=UC(IKL,1)
PE2=UC(IKLAG,I)
CALL AUX(D1,D2,PE1,PE2,X1,X2,X,SX,BX)
S(I)=S(I)+SX
402 B(I)=BX
RETURN
END
SUBROUTINE AUX(D1,D2,PE1,PE2,X1,X2,X,SX,BX)
DEN=-D1*D2*(D1+D2)
A=(-PE1*D2+PE2*(D1+D2))/DEN
B=(PE1*(X**2-X2**2)+PE2*(X1**2-X**2))/DEN
C=(-PE1*X*X2*D2+PE2*X*X1*(D1+D2))/DEN
ZN1=(2./15.)*(3.*X1**2+4.*X1*X+8.*X**2)*SQRT(X-X1)
ZN2=(2./3.)*(X1+2.*X)*SQRT(X-X1)
ZN3=2.*SQRT(X-X1)
SX=A*ZN1+B*ZN2+C*ZN3
BX=(-D1*ZN1+(X2**2-X1**2)*ZN2-X2*D1*X1*ZN3)/DEN
RETURN
END

```

4. PROGRAM TRAJ2

Continuation of calculation of trajectory started by TRAJ1.

```

      PROGRAM TRAJ2(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT,TAPE12
      +,TAPE13)
C
C   THIS PROGRAM CONTINUES THE INTEGRATION OF TRAJECTORY USING THE
C   EXACT SOLUTION FOR CORRECTION FACTORS.  HAMMING'S METHOD IS USED
C   FOR INTEGRATION.
C
      COMMON/T/YA(6),YG(6),Y(4,6),F(4,6),YPP1(6),YM1(6),YPM1(6)
      +,YP1(6),YH(6),YPP(6),SSU,DIS,YPPP(6),CORR(6),YM1A(6),YH1(6)
      +,YO(6),YPO(6),CCD
      COMMON/T3/X,HS,IKLAG,S(4),B(4)
      COMMON/T5/RA,PI,DEF,UE1,UE2,R1,R2,AMU,ANU,G1,G2,FPB,FB,KE1,UB,H2
      COMMON/T6/ZETA1,ZETA2,UP1,UP2,ALAM1P,ALAM2P,R1A,R2A,RAA,UB1
      COMMON/T7/UA1,UA2,ALAM1A,ALAM2A
      COMMON/T9/ITL1
      READ(13,7999) IKLAG,X,H
7999  FORMAT(16,2E17.8)
      READ(13,8000) ((Y(J,I),I=1,6),(F(J,I),I=1,6)),J=1,4)
      READ(13,8000) (CORR(I),I=1,6)
8000  FORMAT(6E17.8)
      ERROR=1.E-03
      R1=50.E-04
      R2=10.E-04
      RA=R2/R1
      HS=0.0A
      DIS=HS*IKLAG
      AMU=0.01
      DEF=1.
      DE1=.0012
      DE2=2.5
      GR=9A1.8
      KONTA=0
      PI=4.*ATAN(1.)
      UB=2.*R1**2*(DEF-DE1)*GR/(9.*AMU)
      FB=6.*PI*AMU*R1*UB
      FPB=FB*RA
      ANU=AMU/DEF
      G1=SQRT(R1*UB)/SQRT(PI*ANU)
      G2=R2*SQRT(UB)/SQRT(R1*PI*ANU)
      H2=RA**2*(DEF-DE2)/(DEF-UE1)
      GF=2.*(DE2-DEF)*R2**2*GR/(9.*AMU*UB)
      AKF=2.*DE2*R2**2*UB/(9.*AMU*R1)
      KE1=R1*UB*DE1/AMU
      IF(Y(4,5).LE.4.) GO TO 550
40   CALL YGRD
      DO 19 I=1,6
      YPP1(I)=YG(I)
      YP1(I)=(1./8.)*(9.*Y(4,I)-Y(2,I)+3.*H*(YPP1(I)+2.*F(4,I)-F(3,I)))
      YP1(I)=YP1(I)-(9./121.)*(YP1(I)-YPPP(I))
19   YH(I)=(YA(I)-YP1(I))/YP1(I)
      DO 20 I=1,6
      IF(ABS(YH(I)).GT.ERROR) GO TO 66
20   CONTINUE
      DO 575 I=1,6
575  CORR(I)=YP1(I)-YPPP(I)
      KONTA=0
      GO TO 63
66   CONTINUE
      KONTA=KONTA+1
      IF(KONTA.LE.3) GO TO 655
C
C   INTEGRATION STEP IS HALVED
C
      X=X-H
83   H=H/2.
      KONTA=0
      DO 185 I=1,6
      YM1(I)=Y(2,I)-H*F(2,I)
185  YA(I)=YM1(I)
14   CALL YGRD
      DO 186 I=1,6
      YPM1(I)=YG(I)
      YM1A(I)=Y(2,I)-(H/2.)*(F(2,I)+YPM1(I))
186  YH1(I)=ABS((YM1A(I)-YM1(I))/YM1A(I))
      DO 187 I=1,6
      IF(YH1(I).GT.ERROR) GO TO 198
187  CONTINUE
      GO TO 88
198  DO 188 I=1,6
      YA(I)=YM1A(I)
188  YM1(I)=YM1A(I)
      GO TO 14
88   DO 12 I=1,6
      J=1
      YM1(I)=YM1A(I)
      YPO(I)=F(2,I)

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12 Y0(I)=Y(2,I)
157 DO 141 I=1,6
    YP1(I)=YM1(I)+2.*H*YPO(I)
    YPPP(I)=YP1(I)
141 YA(I)=YP1(I)
41 CALL YGRD
    DO 16 I=1,6
        YPP1(I)=YG(I)
        YP1(I)=Y0(I)+(H/2.)*(YPO(I)+YPP1(I))
16 YH(I)=(YA(I)-YP1(I))/YP1(I)
    DO 21 I=1,6
        IF(ABS(YH(I)).GT.ERROR) GO TO 67
21 CONTINUE
    GO TO 42
67 DO 31 I=1,6
31 YA(I)=YP1(I)
    GO TO 41
42 IF(J.EQ.2) GO TO 161
48 CALL YGRD
    DO 49 I=1,6
        Y(1,I)=YP1(I)
        F(1,I)=YG(I)
        Y(2,I)=Y(3,I)
        F(2,I)=F(3,I)
        YM1(I)=Y(1,I)
        Y0(I)=Y(2,I)
49 YPO(I)=F(2,I)
    J=J+1
    GO TO 157
161 CALL YGRD
    DO 171 I=1,6
        Y(3,I)=YP1(I)
171 F(3,I)=YG(I)
C
C      INTEGRATION CONTINUES
C
    GO TO 550
655 DO 30 I=1,6
30 YA(I)=YP1(I)
    GO TO 40
63 SS=SSC*R1
    YP55=YP1(5)*R1
    IF((YP55.LE.1.E-07).OR.(SS.LE.1.E-07)) GO TO 33
100 CONTINUE
    DO 70 I=1,6
70 YA(I)=YP1(I)
    DIS=HS*IKLAG
    DIS1=CIS-X
    IF(DIS1.GT.1.E-08) GO TO 199
7000 IKLAG=IKLAG+1
    WRITE(6,1901) IKLAG,ITL1,X,H,CCD
1901 FORMAT(2I6,3E17.8)
    WRITE(6,1902) (YP1(I),I=1,6)
    WRITE(6,1902) ALAM1A,ALAM2A,ALAM1P,ALAM2P
    WRITE(6,1902) (YH(I),I=1,6)
    WRITE(6,1902) UA1,UA2,UP1,UP2
1902 FORMAT(4E17.8)
199 CALL YGRD
    IF(YP1(5).GT.0.7) GO TO 73
    IF(YP1(5).LT.0.3) GO TO 93
    IF(H.LE.0.01) GO TO 245
229 DO 129 I=1,6
    Y(1,I)=Y(2,I)
    Y(2,I)=Y(3,I)
    Y(3,I)=Y(4,I)
    Y(4,I)=YP1(I)
    F(1,I)=F(2,I)
    F(2,I)=F(3,I)
    F(3,I)=F(4,I)
129 F(4,I)=YG(I)
    GO TO 83
93 IF(H.LE.0.005) GO TO 245
    GO TO 229
73 IF(H.GE.0.005) GO TO 245
    DO 121 I=1,6
    IF(ABS(YH(I)).GT.1.E-04) GO TO 245
121 CONTINUE
C
C      INTEGRATION STEP IS DOUBLED
C
    H=2.*H
    DO 131 I=1,6
    Y(4,I)=YP1(I)
    F(4,I)=YG(I)
    Y(2,I)=Y(1,I)
    F(2,I)=F(1,I)
    YM1(I)=Y(2,I)-H*F(2,I)
131 YA(I)=YM1(I)
134 CALL YGRD
    DO 132 I=1,6
    YPM1(I)=YG(I)
    YM1A(I)=Y(2,I)-(H/2.)*(F(2,I)+YPM1(I))
132 YH1(I)=ABS((YM1A(I)-YM1(I))/YM1A(I))
    DO 176 I=1,6

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      IF(YH1(I).GT.ERROR) GO TO 398
176 CONTINUE
      CALL YGRD
      DO 135 I=1,6
        Y(1,I)=YM1A(I)
135 F(1,I)=YG(I)
C
C      INTEGRATION CONTINUES
C
      GO TO 244
398 DO 601 I=1,6
      YA(I)=YP1A(I)
601 YM1(I)=YM1A(I)
      GO TO 134
245 DO 119 I=1,6
      Y(1,I)=Y(2,I)
      Y(2,I)=Y(3,I)
      Y(3,I)=Y(4,I)
      Y(4,I)=YP1(I)
      F(1,I)=F(2,I)
      F(2,I)=F(3,I)
      F(3,I)=F(4,I)
119 F(4,I)=YG(I)
244 IF(DIS1.GT.1.E-08) GO TO 550
      IF(IKLAG.LT.90) GO TO 550
      WRITE(12,468) IKLAG,X,H
468 FORMAT(16,2E17.8)
      WRITE(12,478) ((Y(J,I),I=1,6),(F(J,I),I=1,6)),J=1,4)
      WRITE(12,478) (CORR(I),I=1,6)
478 FORMAT(6E17.8)
550 DO 80 I=1,6
      YP1(I)=Y(1,I)+(4./3.)*H*(2.*F(4,I)-F(3,I)+2.*F(2,I))
      YPPP(I)=YP1(I)
      YYP(I)=YP1(I)+(112./121.)*CORR(I)
      80 YA(I)=YYP(I)
      X=X+H
      GO TO 40
33 WRITE(6,1300) (YP1(I),I=1,6)
      WRITE(6,1300) (YG(I),I=1,6)
      WRITE(6,1300) (YH(I),I=1,6)
      WRITE(6,1300) YP55,SS
1300 FORMAT(1X,6E16.8)
      WRITE(6,1400) ALAM1A,ALAM2A,ALAM1P,ALAM2P
      WRITE(6,1400) UA1,UA2,UP1,UP2
1400 FORMAT(1X,4E16.8)
716 STOP
      END

      SUBROUTINE YGRD
C
C      THIS SUBROUTINE CALCULATES THE DERIVATIVES
C      IN THE EQUATIONS OF MOTION

      COMMON/T/YA(6),YG(6),Y(4,6),F(4,6),YPP1(6),YM1(6),YPM1(6)
      +,YP1(6),YH(6),YYP(6),SSD,DIS,YPPP(6),CORR(6),YM1A(6),YH1(6)
      +,YO(6),YPO(6),CCD
      COMMON/T1/SS1,RP1,RP2,PIP,RAP,FMOL,CF
      COMMON/T3/X,HS,IKLAG,S(4),B(4)
      COMMON/T5/RA,PI,DEF,DE1,DE2,R1,R2,AMU,ANU,G1,G2,FPP,FR,RE1,UB,H2
      COMMON/T6/ZETA1,ZETA2,UP1,UP2,ALAM1P,ALAM2P,R1A,R2A,RAA,UB1
      COMMON/T7/UA1,UA2,ALAM1A,ALAM2A
      UB1=UB
      CCD=SGRT(YA(5)**2+YA(6)**2)
      SSD=CCD-(1.+RA)
      SS=SSC*R1
      Y1=R1**2-R2**2
      D2=(Y1+CCD*R1)**2/(2.*CCD*R1)
      D1=CCD*R1-D2
      Y2=SGRT(D1**2-R2**2)
      AA=Y2
      ZETA1=ALOG((D1+Y2)/R2)
      ZETA2=ALOG((D2+Y2)/R1)
      UP1=(YA(1)*YA(6)-YA(3)*YA(5))/CCD
      ZETA2=-ZETA2
      UP2=(YA(2)*YA(6)-YA(4)*YA(5))/CCD
      UA1=(YA(1)*YA(5)+YA(3)*YA(6))/CCD
      UA2=(YA(2)*YA(5)+YA(4)*YA(6))/CCD
      UAT1=UA1
      UAT2=UA2
      UP1A=UP1
      UP2A=UP2
      R1A=R1
      R2A=R2
      RAA=RA
      CALL FOSOL1
      CALL TOSOL2
      UA1=UAT1
      UA2=UAT2
      UP1=UP1A
      UP2=UP2A
      IF(SS.LT.R1) GO TO 93
      FMOL=0.
      GO TO 94
93 SS1=SS

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```

      RP1=R1
      RP2=R2
      PIP=PI
      RAP=RA
      CALL WOLFORD
94  E1=2.*RE1*(1.+0.5*(DEF/DE1))/9.
      E2=2.*R2**2*UB*LE2*(1.+0.5*(DEF/DE2))/(9.*R1*AMU)
      DO 4005 I=1,4
        S(I)=0.
        B(I)=0.
4005 CONTINUE
      1 YG(1)=(1.-(UA1*ALAM1A*YA(5)/CCD+UP1*ALAM1P*YA(6)/CCD)-G1*S(1)+FMO
        +L*YA(5)/(FB*CCD))/(E1+B(1)*G1)
      YG(2)=(H2-(UA2*ALAM2A*YA(5)/CCD+UP2*ALAM2P*YA(6)/CCD)-G2*S(2)-FMOL
        +YA(5)/(FPB*CCD))/(E2+B(2)*G2)
      YG(3)=((UP1*ALAM1P*YA(5)/CCD-UA1*ALAM1A*YA(6)/CCD)-G1*S(3)+FMOL*YA
        +YA(6)/(FB*CCD))/(E1+B(3)*G1)
      YG(4)=((UP2*ALAM2P*YA(5)/CCD-UA2*ALAM2A*YA(6)/CCD)-G2*S(4)-FMOL*YA
        +YA(6)/(FPB*CCD))/(E2+B(4)*G2)
      YG(5)=YA(2)-YA(1)
      YG(6)=YA(4)-YA(3)
      DIS=C15-X
      IF(DIS1.GT.1.E-08) GO TO 27
      FMOLB=FMOL/FB
      FMOLP=FMOL/FPB
      FMOLB1=(YA(5)*FMOLB)/(CCD*E1)
      FMOLP1=(YA(5)*FMOLP)/(CCD*E2)
      FMOLB2=(YA(6)*FMOLB)/(CCD*E1)
      FMOLP2=(YA(6)*FMOLP)/(CCD*E2)
      WRITE(6,9800) FMOLB1,FMOLP1,FMOLB2,FMOLP2
      WRITE(6,9800) (YG(I),I=1,6)
9800 FORMAT(4E17.8)
      27 RETURN
      END

```

SUBROUTINE TWOSOL1

```

C      THIS SUBROUTINE CALCULATES THE CORRECTION FACTORS
C      FOR THE MOTION ALONG THE LINE OF CENTRES OF TWO SPHERES

      COMMON/T6/ZETA1,ZETA2,UP1,UP2,ALAM1P,ALAM2P,R1A,R2A,RAA,UB1
      COMMON/T7/UA1,UA2,ALAM1A,ALAM2A
      DOUBLE UAN,UBN,UCH,UDN,DET,AN1,BN,CN,DN
      DOUBLE AN(1),AN(2),AN(3),AN(4)
      DIMENSION AN(4)
      UAT1=LA1
      UAT2=LA2
      UA1=-LAT2
      UA2=UAT1
      UA1=UA1*UB1
      UA2=UA2*UB1
      R2=R1A
      R1=R2A
      RA=RAA
      PI=4.*ATAN(1.)
      NRHS=1
      ISCALE=1
      IPRINT=0
      DO 90 I=1,4
90  AN(I)=0.
      SUM1=0.
      SUM2=0.
      ALAM1A=0.
      ALAM2A=0.
      ERROR1=1.E-03
      ITL=10000
      DO 600 MM=1,ITL
      SUM1=ALAM1A
      SUM2=ALAM2A
      N1=4
      RM=MM
      CH1=CCSH((RM-0.5)*ZETA1)
      CH2=CCSH((RM+1.5)*ZETA1)
      SH1=SINH((RM-0.5)*ZETA1)
      SH2=SINH((RM+1.5)*ZETA1)
      CH3=CCSH((RM-0.5)*ZETA2)
      CH4=CCSH((RM+1.5)*ZETA2)
      SH3=SINH((RM-0.5)*ZETA2)
      SH4=SINH((RM+1.5)*ZETA2)
      EXP1=EXP(-(RM-0.5)*ZETA1)
      EXP2=EXP(-(RM+1.5)*ZETA1)
      EXP3=EXP(-(RM-0.5)*ZETA2)
      EXP4=EXP(-(RM+1.5)*ZETA2)
      ANN=(RM*(RM+1.))/(2.*RM+1.)
      CONS1=(SQRT(2.)/2.)*UA1*R1**2*(SINH(ZETA1))*2*ANN*(EXP1/(2.*RM
        +1.)-EXP2/(2.*RM+3.))
      CONS2=(-SQRT(2.)/4.)*UA1*R1**2*(SINH(ZETA1))*2*ANN*(EXP1-EXP2)
      CONS3=(-SQRT(2.)/2.)*UA2*R2**2*(SINH(ZETA2))*2*ANN*(EXP3/(2.*RM
        +1.)-EXP4/(2.*RM+3.))
      CONS4=(-SQRT(2.)/4.)*UA2*R2**2*(SINH(ZETA2))*2*ANN*(EXP3-EXP4)
      ALBE=ZETA1-ZETA2
      S2AB=SH2*CH4-CH2*SH4
      C2AB=CH2*CH4-SH2*SH4

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SAB=SH1*CH3-CH1*SH3
CAB=CH1*CH3-SH1*SH3
P2=RM-0.5
P1=RM+1.5
DET1=(P1**2*SH3*(CH4*SH2-CH2*SH4)+P1*P2*(CH3*(CH4*CH2-SH4*SH2)+
*CH1*(-1.)))
DET2=P1**2*SH1*(SH2*CH4-CH2*SH4)+P1*P2*(CH3*CH1*(SH4*SH2-CH2*
*CH4))
DET3=P1*(SH3*(SH4*SH2-CH2*CH4)+SH1)+P2*CH3*(SH4*CH2-SH2*CH4)
DET4=P1*(SH1*(CH4*CH2-SH4*SH2)-SH3)+P2*CH1*(CH2*SH4-CH4*SH2)
DET=CH1*DET1-CH3*DET2+P2*SH1*DET3-P2*SH3*DET4
UAN=CONS1*DET1-CONS3*DET2+CONS2*DET3-CONS4*DET4
AN1=UAN/DET
UBN=CH1*(P1**2*CONS3*(SH2*CH4-SH4*CH2)-P1*CONS2+P1*CONS4*(CH4*C
+H2-SH4*SH2))-CH3*(P1**2*CONS1*(SH2*CH4-SH4*CH2)+P1*CONS2*(SH4*
+SH2-CH4*CH2)+P1*CONS4)+P2*SH1*(CONS1*P1+CONS4*(CH2*SH4-SH2*CH4)
+P1*CONS3*(SH2*SH4-CH2*CH4))-P2*SH3*(CONS1*P1*(CH2*CH4-SH2*
+SH4)+CONS2*(CH2*SH4-SH2*CH4)-P1*CONS3)
BN=UBN/DET
UCN=CH1*(CONS2*(P1*SH3*CH4-P2*CH3*SH4)+CONS4*(P2*CH1*SH4-P1*CH2
+*SH3)+CONS3*(P1*P2*CH2*CH3-P1*P2*CH1*CH4))-CH3*(CONS2*(P1*SH1*C
+H4-P2*SH2*CH3)+CONS4*(P2*CH1*SH2-P1*CH2*SH1)+CONS1*P1*P2*(CH2*
+CH3-CH1*CH4))+P2*SH1*(CONS3*(P1*SH1*CH4-P2*SH2*CH3)+CONS1*(P2*S
+H4*CH3-P1*SH3*CH4)+CONS4*(SH3*SH2-SH4*SH1))-P2*SH3*(CONS3*(P1*S
+H1*CH2-P2*SH2*CH1)+CONS2*(SH3*SH2-SH4*SH1)+CONS1*(P2*SH4*CH1-P1
+*SH3*CH2))
CN=UCN/DET
UDN=CCONS1*(P1*P2*SH2-P1*P2*SH4*CAB-P2**2*CH4*SAB)+CONS2*(P2*CH4
+*CAB+P1*SH4*SAB-P2*CH2)+CONS3*(P1*P2*SH4+P2**2*CH2*SAB-P1*P2*SH
+2*CAB)+CONS4*(-P1*SH2*SAB-P2*CH4+P2*CH2*CAB)
UN=UDN/DET
998 AN(1)=(2.*RM+1.)*AN1
AN(2)=(2.*RM+1.)*BN
AN(3)=(2.*RM+1.)*CN
AN(4)=(2.*RM+1.)*UN
ALAM1A=((AN(1)+AN(2)+AN(3)+AN(4))*SQRT(2.))/(3.*SINH(ZETA1)*UA1
+*R1**2)+SUM1
ALAM2A=((AN(1)-AN(2)+AN(3)-AN(4))*SQRT(2.))/(3.*SINH(ZETA2)*UA2
+*R2**2)+SUM2
EST1=(ALAM1A-SUM1)/ALAM1A
EST2=(ALAM2A-SUM2)/ALAM2A
IF (ABS(EST1).LE.ERROR1).AND.(ABS(EST2).LE.ERROR1) GO TO 103
600 CONTINUE
103 ALAM1=ALAM1A
ALAM2=ALAM2A
ALAM1A=ALAM1
ALAM2A=ALAM2
RETURN
END

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SUBROUTINE TWOSOL2

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C THIS SUBROUTINE CALCULATES THE CORRECTION FACTORS FOR
C MOTION PERPENDICULAR TO THE LINE OF CENTRES OF TWO SPHERES

COMMON/T4/ITL,H(250,2),CC(500),C(500,7),ALIN(2,7),ALIN1(2),G(1,4
1),KONT,IND
COMMON/T8/M,R(8)
COMMON/T6/ZETA1,ZETA2,UP1,UP2,ALAM1P,ALAM2P,R1A,R2A,RAA,UB1
COMMON/T9/ITL1
UA1=UP2
UA2=UP1
UA1=UA1+UB1
UA2=UA2+UB1
R1=R1A
R2=R2A
RA=RAA
PI=4.*ATAN(1.)
111 DO 777 I=1,4
777 G(1,I)=0.
DO 888 I=1,250
DO 888 J=1,2
888 H(I,J)=0.
DO 9047 I=1,500
DO 9047 J=1,7
9047 C(1,J)=0.
ERROR1=1.E-03
KONT=1
ITL=15
1030 DO 1 M=KONT,ITL
CALL RR
IND=1
CALL AB
1 CONTINUE
Z02=COSH(ZETA2/2.)
Q12=SINH(1.5*ZETA2)
Z01=COSH(0.5*ZETA1)
Q11=SINH(1.5*ZETA1)
B01=TANH(0.5*ZETA1)
B02=TANH(0.5*ZETA2)
B0=B01-B02
EXP1=EXP(-0.5*ZETA1)

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EXP2=EXP(0.5*ZETA2)
Z11=CCSH(1.5*ZETA1)
Z12=CCSH(1.5*ZETA2)
SIN1=SINH(ZETA1)
SIN2=SINH(ZETA2)
EO=(2.*H(1,1)*(B01*Q12/(Z02*SIN2)-B02*Q11/(Z01*SIN1)))/(3.*B0)+(2.
+*H(1,2)*(B01*Z12/(Z02*SIN2)-B02*Z11/(Z01*SIN1)))/(3.*B0)+(2.
+*SQRT(2.)*(B01*UA2*EXP2/Z02-B02*UA1*EXP1/Z01))/B0
FO=(2.*H(1,1)*(G11/(SIN1*Z01)-G12/(SIN2*Z02)))/(3.*B0)+(2.*H(1,2)*
+(Z11/(SIN1*Z01)-Z12/(SIN2*Z02)))/(3.*B0)+(2.*SQRT(2.)*(UA1*EX
+P1/Z01-UA2*EXP2/Z02))/B0
SUME=EO
SUMF=FO
CALL GAUSS2
IND=2
DO 2 M=1,ITL
CALL RR
CALL AB
SUME=SUME+G(1,3)
2 SUMF=SUMF+G(1,4)
SUMEE=SQRT(2.)*SIN1*(SUME+SUMF)/(3.*UA1)
SUMFF=-SQRT(2.)*SIN2*(SUME-SUMF)/(3.*UA2)
IF(KONT.EQ.1) GO TO 335
RAT1=(SUMEE-ALAM1)/SUMEE
RAT2=(SUMFF-ALAM2)/SUMFF
IF((ABS(RAT1).LT.ERROR1).AND.(ABS(RAT2).LT.ERROR1)) GO TO 980
333 ALAM1=SUMEE
ALAM2=SUMFF
KONT=ITL
ITL=ITL+15
IF(ITL.GE.250) GO TO 33
SUMF=0.
SUME=0.
L=2*KONT-3
DO 555 J=1,7
C(L,J)=ALIN(1,J)
555 C(L+1,J)=ALIN(2,J)
CC(L)=ALIN1(1)
CC(L+1)=ALIN1(2)
GO TO 1030
980 CONTINUE
ALAM1P=ALAM2
ALAM2P=ALAM1
ITL1=ITL
33 RETURN
END

SUBROUTINE RR
COMMON/T8/M,R(8)
AM=M
R(1)=AM+2.
R(2)=2.*AM+3.
R(3)=AM+1.
R(4)=AM-1.
R(5)=2.*AM+1.
R(6)=AM-2.
R(7)=AM+3.
R(8)=2.*AM-1.
RETURN
END

C
C
C
C
SUBROUTINE AB
THIS SUBROUTINE CALCULATES THE COEFFICIENTS IN MATRIX AB AND
REARRANGES THE ELEMENTS INTO A BAND MATRIX OF BREADTH 7
COMMON/T4/ITL,H(250,2),CC(500),C(500,7),ALIN(2,7),ALIN1(2),G(1,4
1),KONT,IND
COMMON/T8/M,R(8)
COMMON/T6/ZETA1,ZETA2,UP1,UP2,ALAM1P,ALAM2P,R1A,R2A,RAA,UB1
DIMENSION W(12)
UA1=UP2
UA2=UP1
AM=M
UA1=UA1*UB1
UA2=UA2*UB1
B01=TANH((AM+0.5)*ZETA1)
B02=TANH((AM+0.5)*ZETA2)
B0=B01-B02
COTH1=COTH(ZETA1)
COTH2=COTH(ZETA2)
QMZO=((1./B02)*COTH1-(1./B01)*COTH2)/((1./B02)-(1./B01))
ZMZO=((1./B01)*(1./B02)*(COTH1-COTH2)-(1./B02)+(1./B01))/((1./B0
+2)-(1./B01))
QPZORC=(COTH1+(1./B01)-COTH2-(1./B02))/((1./B02)-(1./B01))
ZPZORC=(COTH1*(1./B01)-COTH2*(1./B02))/((1./B02)-(1./B01))
QMZOORC=(COTH1-(1./B01)-COTH2+(1./B02))/((1./B02)-(1./B01))
ZMZOORC=(COTH1*(1./B01)-COTH2*(1./B02))/((1./B02)-(1./B01))
EEEF=2.*(AM+1.5)*ZETA1
EEEM=2.*(AM-0.5)*ZETA1
EEEN=2.*(AM+0.5)*ZETA1
EEEI=2.*(AM-0.5)*ZETA2
EEEO=2.*(AM+0.5)*ZETA2
EEFI=2.*(AM+1.5)*ZETA2

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      IF(ABS(EEE1P).GT.200.) GO TO 1237
      TITIP=2./(1.+EXP(-EEE1P))
      GO TO 1238
1237 TITIP=0.
1238 IF(ABS(EEE10).GT.200.) GO TO 1239
      TITIO=2./(1.+EXP(-EEE10))
      GO TO 1240
1239 TITIO=0.
1240 IF(ABS(EEE1M).GT.200.) GO TO 1241
      TITIM=2./(1.+EXP(-EEE1M))
      GO TO 1242
1241 TITIM=0.
1242 IF(EEE0.GT.200.) GO TO 1243
      AMINIO=2./(1.+EXP(EEE0))
      GO TO 1244
1243 AMINIO=0.
1244 IF(EEEP.GT.200.) GO TO 1245
      AMINIP=2./(1.+EXP(EEEP))
      GO TO 1246
1245 AMINIP=0.
1246 IF(EEEM.GT.200.) GO TO 1247
      AMINIM=2./(1.+EXP(EEEM))
      GO TO 1248
1247 AMINIM=0.
1248 CONTINUE
      IF(INC.EQ.1) GO TO 20
      IF(M.EQ.1) GO TO 300
      IF(M.EQ.ITL) GO TO 400
      G(1,1)=-2.*H(M+1,1)*QPZOBO*(1)/(1.*R(2))-2.*H(M+1,2)*
      +ZPZOBC*(1)/(1.*R(2))+H(M,1)*2.*BO1*BO2*(COTH1-COTH2)/BO
      +H(M,2)*2*(COTH1*BO2-COTH2*BO1)/BO-H(M-1,1)*2.*QM
      +ZOBO*(4)/(1.*R(8))-H(M-1,2)*2.*ZMZOB*(4)/(1.*R(8))
      GO TO 20
300 G(1,1)=-2.*H(M+1,1)*QPZOBO*(1)/(1.*R(2))-2.*H(M+1,2)*ZPZOBO
      +R(1)/(1.*R(2))+H(M,1)*2.*BO1*BO2*(COTH1-COTH2)/BO+H(M,2)*2.*
      +COTH1*BO2-COTH2*BO1)/BO
      GO TO 20
400 G(1,1)=H(M,1)*2.*BO1*BO2*(COTH1-COTH2)/BO+H(M,2)*2*(COTH1*
      +BO2-COTH2*BO1)/BO-H(M-1,1)*2.*QMZOBU*(4)/(1.*R(8))-H(M-1,2)*2
      +.*ZMZOB*(4)/(1.*R(8))
20 ZPZO=((1./BO1)*(1./BO2)*(COTH1-COTH2)+(1./BO2)-(1./BO1))/((1.
      +/BO2)-(1./BO1))
      QPZO=((1./BO2)*COTH1-(1./BO1)*COTH2)/((1./BO2)-(1./BO1))
      IF(INC.EQ.1) GO TO 21
      IF(M.EQ.1) GO TO 301
      IF(M.EQ.ITL) GO TO 401
      G(1,2)=2.*R(1)*H(M+1,1)*QPZO/(R(2)*1.)+2.*R(1)*H(M+1,2)*ZPZO/(R(2)
      +*1.)+2.*H(M,1)*(COTH2*BO2-COTH1*BO1)/BO+2.*H(M,2)*(COTH2-C
      +OTH1)/BO+H(M-1,1)*2.*R(4)*QMZO/(R(8)*1.)+H(M-1,2)*2.*R(4)*
      +ZMZO/(R(8)*1.)
      GO TO 21
301 G(1,2)=2.*R(1)*H(M+1,1)*QPZO/(R(2)*1.)+2.*R(1)*H(M+1,2)*ZPZO/
      +R(2)*1.)+2.*H(M,1)*(COTH2*BO2-COTH1*BO1)/BO+2.*H(M,2)*(COTH2-
      +COTH1)/BO
      GO TO 21
401 G(1,2)=2.*H(M,1)*(COTH2*BO2-COTH1*BO1)/BO+2.*H(M,2)*(COTH2-CO
      +TH1)/BO+H(M-1,1)*2.*R(4)*QMZO/(R(8)*1.)+H(M-1,2)*2.*R(4)*ZMZO/
      +(R(8)*1.)
21 CONTINUE
      IF(INC.EQ.1) GO TO 22
      IF(M.EQ.1) GO TO 302
      IF(M.EQ.ITL) GO TO 402
      G(1,3)=-H(M+1,1)*R(1)*R(3)*QPZOBO/(R(2)*1.)-H(M+1,2)*R(3)*R(1)*
      +ZPZOBC/(R(2)*1.)+H(M-1,1)*AM*R(4)*QMZOBU/(R(8)*1.)+H(M-1,2
      +)*ZMZOB*AM*R(4)/(R(8)*1.)+2.*SQRT(2.)*(BO1*UA2*TITIO
      +/1.-BO2*UA1*AMINIO/1.)/BO
      GO TO 14
302 G(1,3)=-H(M+1,1)*R(1)*R(3)*QPZOBO/(R(2)*1.)-H(M+1,2)*R(3)*R(1)
      +ZPZOBO/(R(2)*1.)+2.*SQRT(2.)*(BO1*UA2*TITIO/1.
      +BO2*UA1*AMINIO/1.)/BO
      GO TO 14
402 G(1,3)=H(M-1,1)*AM*R(4)*QMZOBU/(R(8)*1.)+H(M-1,2)*AM*R(4)*
      +ZMZOB/(R(8)*1.)+2.*SQRT(2.)*(BO1*UA2*TITIO/1.
      +BO2*UA1*AMINIO/1.)/BO
14 CONTINUE
      IF(M.EQ.1) GO TO 303
      IF(M.EQ.ITL) GO TO 403
      G(1,4)=H(M+1,1)*R(3)*R(1)*QPZO/(R(2)*1.)+H(M+1,2)*R(3)*R(1)*ZPZO
      +/(R(2)*1.)-H(M-1,1)*AM*R(4)*QMZO/(R(8)*1.)-H(M-1,2)*AM*R(4)
      +)*ZMZC/(1.*H(8))+2.*SQRT(2.)*(UA1*AMINIO
      +/1.-UA2*TITIO/1.)/BO
      GO TO 9
303 G(1,4)=H(M+1,1)*R(3)*R(1)*QPZO/(R(2)*1.)+H(M+1,2)*R(3)*R(1)*
      +ZPZO/(R(2)*1.)+2.*SQRT(2.)*(UA1*AMINIO/1.-UA2
      +*TITIO/1.)/BO
      GO TO 9
403 G(1,4)=-H(M-1,1)*AM*R(4)*QMZO/(R(8)*1.)-H(M-1,2)*AM*R(4)*ZMZO
      +/(1.*R(8))+2.*SQRT(2.)*(UA1*AMINIO/1.-UA2*
      +TITIO/1.)/BO
9 CONTINUE
      RETURN
22 BM1=TANH((AM-0.5)*ZETA1)
      BM2=TANH((AM-0.5)*ZETA2)
      BP1=TANH((AM+1.5)*ZETA1)
      BP2=TANH((AM+1.5)*ZETA2)

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BM=BM1-BM2
BP=BP1-BP2
QOZM=((1./BM2)*COTH1-(1./BM1)*COTH2)/((1./BM2)-(1./BM1))
QOZP=((1./BP2)*COTH1-(1./BP1)*COTH2)/((1./BP2)-(1./BP1))
ZOZP=((1./BP1)*(1./BP2)*(COTH1-COTH2)-(1./BP2)+(1./BP1))
+/(1./BP2)-(1./BP1))
ZOZM=((1./BM1)*(1./BM2)*(COTH1-COTH2)+(1./BM2)-(1./BM1))/
+((1./BM2)-(1./BM1))
QOZMBM=(COTH1+(1./BM1)-COTH2-(1./BM2))/((1./BM2)-(1./BM1))
QOZPBP=(COTH1-(1./BP1)-COTH2+(1./BP2))/((1./BP2)-(1./BP1))
ZOZPBP=(COTH1*(1./BP1)-COTH2*(1./BP2))/((1./BP2)-(1./BP1))
ZOZMBM=(COTH1*(1./BM1)-COTH2*(1./BM2))/((1./BM2)-(1./BM1))
A01=10.*B01*B02*(COTH1-COTH2)/B0+2.*R(4)*R(3)*QOZMBM/(1.*R(5))-2.*
+AM*R(1)*QOZPBP/(R(5)*1.)+AM*R(3)*QOZMBM/(R(5)*1.)-AM*R(3)*
+QOZPBP/(R(5)*1.)+R(6)*R(4)*QOZMBM/(R(5)*1.)-R(1)*R(7)*QOZ
+PBP/(R(5)*1.)+2.*R(5)
B001=10.*(COTH1*B02-COTH2*B01)/B0+2.*R(4)*R(3)*ZOZMBM/(R(5)*1.)-2.*
+AM*R(1)*ZOZPBP/(R(5)*1.)+AM*R(3)*ZOZMBM/(R(5)*1.)-AM*R(3)*
+ZOZPBP/(R(5)*1.)+R(6)*R(4)*ZOZMBM/(R(5)*1.)-R(1)*R(7)*ZOZ
+PBP/(R(5)*1.)
A02=10.*(COTH2*B02-COTH1*B01)/B0+2.*R(4)*R(3)*QOZM/(R(5)*1.)+2.*AM
+R(1)*QOZP/(R(5)*1.)-AM*R(3)*QOZM/(R(5)*1.)+AM*R(3)*QOZP/(
+R(5)*1.)-R(4)*R(6)*QOZM/(R(5)*1.)+R(1)*R(7)*QOZP/(R(5)*1.)
B002=10.*(COTH2-COTH1)/B0+2.*R(4)*R(3)*ZOZM/(R(5)*1.)+2.*AM*R(1)*
+ZOZP/(R(5)*1.)-AM*R(3)*ZOZM/(R(5)*1.)+AM*R(3)*ZOZP/(R(5)*1.)
+R(1)*R(7)*ZOZP/(R(5)*1.)-R(6)*R(4)*ZOZM/(R(5)*1.)+2.*R(
+5)
IF(M.EQ.1) GO TO 1
IF(M.EQ.ITL) GO TO 2
AA1=-10.*R(4)*QMZOBO/(R(8)*1.)+2.*R(4)*BM1*BM2*(COTH2-CO
+TH1)/BM+2.*AM*R(4)*QMZOBO/(R(8)*1.)+2.*R(4)*R(1)*QMZOBO/(R
+(8)*1.)-2.*R(4)
AA2=10.*R(4)*QMZO/(R(8)*1.)+2.*R(4)*(COTH1*BM1-COTH2*BM2)/BM-2.*AM
+R(4)*QMZO/(R(8)*1.)-2.*R(4)*R(1)*QMZO/(R(8)*1.)
BB1=-10.*R(4)*ZMZOB0/(R(8)*1.)+2.*R(4)*(COTH2*BM1-COTH1*BM2)/BM+2.*
+AM*R(4)*ZMZOB0/(R(8)*1.)+2.*R(4)*R(1)*ZMZOB0/(R(8)*1.)
BB2=10.*R(4)*ZMZ0/(R(8)*1.)+2.*R(4)*(COTH1-COTH2)/BM-2.*AM*R(4)*ZM
+ZO/(R(8)*1.)-2.*R(4)*R(1)*ZMZ0/(R(8)*1.)-2.*R(4)
A11=-10.*R(1)*QPZORO/(R(2)*1.)+2.*R(1)*BP1*BP2*(COTH1-COTH2)/BP-2.*
+R(3)*R(1)*QPZOB0/(R(2)*1.)-2.*R(4)*R(1)*QPZOB0/(R(2)*1.)-
+2.*R(1)
B11=-10.*R(1)*ZPZOBO/(R(2)*1.)+2.*R(1)*(COTH1*BP2-COTH2*BP1)/BP-2.*
+R(3)*R(1)*ZPZOBO/(R(2)*1.)-2.*R(4)*R(1)*ZPZOBO/(R(2)*1.)
A22=10.*R(1)*QPZO/(R(2)*1.)+2.*R(1)*(COTH2*BP2-COTH1*BP1)/BP+2.*R(
+1)*R(3)*QPZO/(R(2)*1.)+2.*R(4)*R(1)*QPZO/(R(2)*1.)
B22=10.*R(1)*ZPZO/(R(2)*1.)+2.*R(1)*(COTH2-COTH1)/BP+2.*R(3)*R(
+1)*ZPZO/(R(2)*1.)+2.*R(4)*R(1)*ZPZO/(R(2)*1.)-2.*R(1)
Q(1)=B11
Q(2)=A11
Q(3)=B001
Q(4)=A01
Q(5)=BB1
Q(6)=AA1
Q(7)=B22
Q(8)=A22
Q(9)=B002
Q(10)=A02
Q(11)=BB2
Q(12)=AA2
I=2*M-1
DO 12 J=1,6
L=8-J
C(I,L)=J(J)
12 C(I+1,L-1)=Q(J+6)
CC(I)=4.*SQRT(2.)*(UA2*B01*TITIO/1.-UA1*B02*
+AMINIC/1.)/B0+2.*SQRT(2.)*(-UA2*BM1*TITIM
+/1.+UA1*BM2*AMINIM/1.)/BM+2.*SQ
+RT(2.)*(-UA2*BP1*TITIP/1.+UA2*BP2*
+AMINIP/1.)/BP
CC(I)=-CC(I)
CC(I+1)=4.*SQRT(2.)*(UA1*AMINIO/1.-UA2*TITIO
+/1.)/B0+2.*SQRT(2.)*(-UA1*AMINIM
+/1.+UA2*TITIM/1.)/BM+2.*SQRT(2.)*(-UA1*
+AMINIP/1.+UA2*TITIP/1.)/BP
CC(I+1)=-CC(I+1)
GO TO 3
1 A11=-10.*R(1)*QPZORO/(1.*R(2))+2.*R(1)*BP1*BP2*(COTH1-COTH2)/BP-
+2.*R(3)*R(1)*QPZOB0/(R(2)*1.)-2.*R(4)*R(1)*QPZOB0/(R(2)*1.)-
+2.*R(1)
B11=-10.*R(1)*ZPZOBO/(R(2)*1.)+2.*R(1)*(COTH1*BP2-COTH2*BP1)/BP-2.*
+R(3)*R(1)*ZPZOBO/(R(2)*1.)-2.*R(4)*R(1)*ZPZOBO/(R(2)*1.)
A22=10.*R(1)*QPZO/(R(2)*1.)+2.*R(1)*(COTH2*BP2-COTH1*BP1)/BP+2.*
+R(1)*R(3)*QPZO/(R(2)*1.)+2.*R(4)*R(1)*QPZO/(R(2)*1.)
B22=10.*R(1)*ZPZO/(R(2)*1.)+2.*R(1)*(COTH2-COTH1)/BP+2.*R(3)*R(1)*
+ZPZO/(R(2)*1.)+2.*R(4)*R(1)*ZPZO/(R(2)*1.)-2.*R(1)
Q(1)=B11
Q(2)=A11
Q(3)=B001
Q(4)=A01
Q(5)=B22
Q(6)=A22
Q(7)=B002
Q(8)=A02
DO 10 J=1,4
L=8-J

```

```

      K=L-1
      C(M,L)=Q(J)
10  C(M+1,K)=Q(J+4)
      CC(M)=4.*SQRT(2.)*(UA2*BO1*TITIO/1.-UA1*BO2*
+AMINIC/1.)/BO+2.*SQRT(2.)*(-UA2*BM1*TITIM
+/1.+UA1*BM2*AMINIM/1.)/BM+2.*SQRT
+(2.)*(-UA2*BP1*TITIP/1.+UA1*BP2*AMINIP
+/1.)/BP
      CC(M)=-CC(M)
      CC(M+1)=4.*SQRT(2.)*(UA1*AMINIO/1.-UA2*TITIO
+/1.)/BO+2.*SQRT(2.)*(-UA1*AMINIM
+/1.+UA2*TITIM/1.)/BM+2.*SQRT(2.)*(-UA1*
+AMINIP/1.+UA2*TITIP/1.)/BP
      CC(M+1)=-CC(M+1)
      GO TO 3
2  AA1=-10.*R(4)*QMZOBO/(R(8)*1.)+2.*R(4)*BM1*BM2*(COTH2-COTH1)/BM
+2.*AMR(4)*QMZOBO/(R(8)*1.)+2.*R(4)*R(1)*QMZOBO/(R(8)*1.)-2
+.R(4)
      AA2=10.*R(4)*QMZO/(R(8)*1.)+2.*R(4)*(COTH1*BM1-COTH2*BM2)/BM-2.*AM
+R(4)*QMZO/(R(8)*1.)-2.*R(4)*R(1)*QMZO/(R(8)*1.)
      BB1=-10.*R(4)*ZMZOB0/(R(8)*1.)+2.*R(4)*(COTH2*BM1-COTH1*BM
+2)/BM+2.*AMR(4)*ZMZOB0/(R(8)*1.)+2.*R(4)*R(1)*ZMZOB0/(R(8)*1.)
      BB2=10.*R(4)*ZMZ0/(R(8)*1.)+2.*R(4)*(COTH1-COTH2)/BM-2.*AMR(4)*ZM
+ZO/(R(8)*1.)-2.*R(4)*R(1)*ZMZ0/(R(8)*1.)-2.*R(4)
      Q(1)=B001
      Q(2)=A01
      Q(3)=B01
      Q(4)=A01
      Q(5)=B002
      Q(6)=A02
      Q(7)=B02
      Q(8)=AA2
      IL=2*M-1
      DO 11 J=1,4
      L=6-J
      K=L-1
      C(IL,L)=Q(J)
11  C(IL+1,K)=Q(J+4)
      CC(IL)=4.*SQRT(2.)*(UA2*BO1*TITIO/1.-UA1*BO2*
+AMINIC/1.)/BO+2.*SQRT(2.)*(-UA2*BM1*TITIM
+/1.+UA1*BM2*AMINIM/1.)/BM+2.*SQRT(
+2.)*(-UA2*BP1*TITIP/1.+UA1*BP2*AMINIP
+/1.)/BP
      CC(IL)=-CC(IL)
      CC(IL+1)=4.*SQRT(2.)*(UA1*AMINIO/1.-UA2*TITIO
+/1.)/BO+2.*SQRT(2.)*(-UA1*
+AMINIM/1.+UA2*TITIM/1.)/BM+2.*SQRT(2.)*(-UA1*
+AMINIP/1.+UA2*TITIP/1.)/BP
      CC(IL+1)=-CC(IL+1)
3  RETURN
END

C
C      SUBROUTINE GAUSS2
C
C      THIS SUBROUTINE DOES THE GAUSSIAN ELIMINATION
C
      COMMON/T4/ITL,H(250,2),CC(500),C(500,7),ALIN(2,7),ALIN1(2),G(1,4
1),KONT,IND
      DIMENSION AX(505)
      DO 100 J=1,505
100  AX(J)=0.
      IF(KONT.NE.1) GO TO 6
      I=1
      GO TO 5
6  I=2*M*CHT-3
      N=2*ITL
      DIV=C(I+1,3)/C(I,4)
      DO 10 J=4,6
10  C(I+1,J)=C(I+1,J)-DIV*C(I,J+1)
      CC(I+1)=CC(I+1)-DIV*CC(I)
      C(I+1,3)=0.
      IF(I.EQ.(N-1)) GO TO 300
      DIV=C(I+2,2)/C(I,4)
      DO 20 J=3,5
20  C(I+2,J)=C(I+2,J)-DIV*C(I,J+2)
      CC(I+2)=CC(I+2)-DIV*CC(I)
      C(I+2,2)=0.
      IF(I.EQ.(N-2)) GO TO 667
      GO TO 337
667 DO 1040 L=1,7
1040 ALIN(2,L)=C(I,L)
      ALIN1(2)=CC(I)
      937 IF((I/2)*2).NE.I) GO TO 180
      I=I+1
      GO TO 2
180 DIV=C(I+3,1)/C(I,4)
      DO 30 J=2,4
30  C(I+3,J)=C(I+3,J)-DIV*C(I,J+3)
      CC(I+3)=CC(I+3)-DIV*CC(I)
      C(I+3,1)=0.

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```

      IF(I.EQ.(N-3)) GO TO 666
      GO TO 321
666  DO 1020 L=1,7
1020  ALIN(I,L)=C(I,L)
      ALIN1(I)=CC(I)
321  I=I+1
      GO TO 2
300  I=I+1
      AX(I)=CC(I)/C(I,4)
      N1=2*ITL
      DO 8 I=1,N1-1
      L=N1-I
      8 AX(L)=(CC(L)-AX(L+1)*C(L,5)-AX(L+2)*C(L,6)-AX(L+3)*C(L,7))/C(L,4)
      DO 999 I=1,ITL
      K=(2*I-1)
      H(I,1)=AX(K)
999  H(I,2)=AX(K+1)
      RETURN
      END

      SUBROUTINE MOLFORC

C      THIS SUBROUTINE CALCULATES THE SUM OF REPULSIVE
C      AND ATTRACTIVE FORCES

      COMMON/T1/SS1,RP1,RP2,PIP,RAP,FMOL,CF
      SS=SS1
      R1=RP1
      R2=RP2
      P1=PIP
      RA=RAP
      PS01=0.06
      PS02=0.06
      ZP=1.
      ZM=1.
      ANM=1.E-12
      ANIP=1.E-12
      EC=4.803250E-10
      AN=6.02217E+23
      TE=298.
      DEC=79.
      BOK=1.38062E-16
      AK=SQRT(4.*PI*EC**2*AN*(ANM*ZM**2+A(IP*ZP**2)/(DEC*BOK*TE)))
      EXPS=EXP(-AK*SS)
      FR=78.E-04/9.*R1*R2*(PS01**2+PS02**2)*((2.*PS01*PS02*(-2.*AK*EXP
15) )/(PS01**2+PS02**2)*(1.-EXPS**2))+2.*AK*EXPS**2/(1.-EXPS**2))/(
24.*(R1+R2))
799  CONTINUE
      SSD=SS/R1
      CCD=1.+RA+SSO
      ST1=SSD**2+2.*SSD+2.*RA*SSD
      ST2=SSD**2+4.*RA+2.*RA*SSD+2.*SSD
      A132=1.E-13
      CALL LONDON
      FAT=(2.*A132)*RA*CCD/(3.*R1)*(1./ST1**2+1./ST2**2-2./(ST1*ST2))*CF
      FMOL=FR+FAT
      RETURN
      END

      SUBROUTINE LONDON

C      THIS SUBROUTINE CALCULATES THE CORRECTION FACTOR FOR
C      LONDON-VAN DER WAALS FORCES DUE TO RETARDATION

      COMMON/T1/SS1,RP1,RP2,PIP,RAP,FMOL,CF
      SS=SS1
      R1=RP1
      R2=RP2
      P1=PIP
      RA=RAP
      AL=0.1E-04
      P=SS*2.*PI/AL
      CONS=AL/(2.*P1)
      SSD=SS/R1
      C=SS+R1+R2
      D=R2**2-C**2
      A=2.45*CONS
      B=2.17*(CONS**2)
      Q=0.59*CONS**3
      H1=A/30.
      H2=B/50.
      H3=A*C/15.
      H4=A*C/50.
      H5=B*C/50.
      H6=R*R1/60.
      H7=Q/210.
      H8=B*C/180.
      H9=C*C/315.
      H10=Q*0/420.

```

```

S1=-H3+H1*R1-H2
T1=H3+H1*R1+H2
S2=-H4-H3*R1+H5-5.*H1*R1**2/2.-H6+H7
T2=H4-H3*R1-H5+5.*H1*R1**2/2.-H6-H7
S3=H8+H5*R1**2+2.*H5*R1-2.*H9+H1*R1**3+7.*H6*R1/3.+2.*H7*R1-2.*H4*
+R1
T3=-H8-H3*R1**2+2.*H5*R1+2.*H9+H1*R1**3-7.*H6*R1/3.+2.*H7*R1-2.*H4*
+R1
S4=-H10-2.*H5*R1**2-6.*H9*R1-H6*R1**2-9.*H7*R1**2/2.+3.*H8*R1
T4=H10+2.*H5*R1**2-6.*H9*R1-H6*R1**2+9.*H7*R1**2/2.+3.*H8*R1
S5=6.*H9*R1**2+2.*H7*R1**3-4.*H10*R1
T5=-6.*H9*R1**2+2.*H7*R1**3-4.*H10*R1
S22=H3/2.-2.*H1*R1+H2
T22=-H3/2.-2.*H1*R1-H2
S33=-2.*H5/3.+2.*H1*R1**2+2.*H6-4.*H7/3.+H3*R1
T33=2.*H5/3.-2.*H1*R1**2+2.*H6+4.*H7/3.+H3*R1
S44=3.*H9/2.-2.*H6*R1-4.*H7*R1-2.*H5*R1
T44=-3.*H9/2.+2.*H6*R1-4.*H7*R1-2.*H5*R1
S55=6.*H9*R1+4.*H7*R1**2
T55=6.*H9*R1-4.*H7*R1**2
U1=1./(C+P2+R1)
V1=1./(C-P2+R1)
U2=1./(C+R2-R1)
V2=1./(C-R2-R1)
G1=SSD**2+2.*RA*SSD+2.*SSD
G2=G1+4.*PA
FN=-2.*((SSD*RA+1.)*(-RA/G1**2-RA/G2**2+2.*RA/(G1*G2)))/(3.*R1)
IF(P,GT.2.) GO TO 20
FR1=(-R1*R2*(-1./((SS**2*(1.+1.77*P))-1.77*2.*PI/(AL*SS*(1.+1.77*P)
1**2)))/(6.*(R1+R2))
IF(P,LT.0.5) GO TO 10
20 FR2=(-(U1-V1)*(-2.*H1/C-S1/C**2)+(U2-V2)*(2.*H1/C-T1/C**2)+(U1**2
+-V1**2)*(-S1/C+S22/C-S2/C**2)+(U2**2-V2**2)*(-T1/C+T22/C-T2/C
**2)+(U1**3-V1**3)*(-2.*S2/C+S33/C-S3/C**2)+(U2**3-V2**3)*
+(-2.*T2/C+T33/C-T3/C**2)+(U1**4-V1**4)*(-3.*S3/C+S44/C-S4/
+C**2)+(U2**4-V2**4)*(-3.*T3/C+T44/C-T4/C**2)+(U1**5-V1*
**5)*(-4.*S4/C+S55/C-S5/C**2)+(U2**5-V2**5)*(-4.*T4/C+T55/C-
+T5/C**2)-5.*S5*(U1**6-V1**6)/C-5.*T5*(U2**6-V2**6)/C-8.*H1
+R1*R2*U1*U2*V1*V2-H1*(ALOG(U1*V2/(V1*U2)))/C**2)
IF((P,GE.0.5).AND.(P,LE.2.)) GO TO 50
IF(P,GT.2.) GO TO 30
10 CF1=FR1/FN
CF=CF1
RETURN
30 CF2=FR2/FN
CF=CF2
RETURN
50 CF=(FR1+FR2)/(2.*FN)
RETURN
END
FUNCTION SINH(X)
SINH=(EXP(X)-EXP(-X))/2.
RETURN
END
FUNCTION COSH(X)
COSH=(EXP(X)+EXP(-X))/2.
RETURN
END
FUNCTION COTH(X)
COTH=(EXP(X)+EXP(-X))/(EXP(X)-EXP(-X))
RETURN
END

```

5. PROGRAM VIRTUAL

Calculation of kinetic energy.

```

      PROGRAM VIRTUAL(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
C
C      THIS PROGRAM CALCULATES THE KINETIC ENERGY OF ONE
C      SPHERE IN A TWO SPHERES SYSTEM MOVING IN A FLUID.
C
      COMMON/T/IS(2),YE(1),XMU,YMU(1),YH(1),YG(1),YD(1),YS(1),N,YEI,HS,H
      *MIN,H,ZETA1,ZETA2,PI,IT,DE,ERR1,AA
      DOUBLE YS,YU
      ERROR=1.E-05
      ERK1=ERROR
      READ,X,NN,IT
      ANN=NN
      READ,IS(2)
      N=1
      DE=1.
      R1=1.
      H2=R1
      Y=X+2.
      Y1=R2**2-R1**2
      D2=(Y1+Y**2*R2**2)/(2.*Y*R2)
      D1=(Y*R2-D2)
      Y2=SQRT(D1**2-R1**2)
      ZETA1=ALOG((D1+Y2)/R1)
      ZETA2=ALOG((D2+Y2)/R2)
      ZETA2=-ZETA2
      AA=SQRT(D1**2-R1**2)
      UA1=1.
      YE(1)=ERRDR
      XMU=-1.
      YMU(1)=0.
      IS(1)=1
      YE1=0.03
      PI=4.*ATAN(1.)
      HS=2./ANN
      HMIN=1.E-16
      H=0.1
      YD(1)=0.
      K=0
      DO 146 I=1,NN
60    CALL SINT
      IF(IS(1).EQ.2) GO TO 60
      IF(IS(1).LE.3) GO TO 146
      WRITE(6,178) IS(1)
178   FORMAT(I3)
      STOP
146   PRINT,XMU,YMU
      STOP
      END
      SUBROUTINE SINT
      COMMON/T/IS(2),YE(1),XMU,YMU(1),YH(1),YG(1),YD(1),YS(1),N,YEI,HS,
      *MIN,H,ZETA1,ZETA2,PI,IT,DE,ERR1,AA
      DOUBLE YS,YU
      IF((IS(1).LE.1).OR.(K.LE.0).OR.(H.NE.HH))GO TO 1
      GO TO 4
1     K=1
      HH=HS
2     IF(HH.LE.H) GO TO 3
      HH=0.5*HH
      K=2*K
      GO TO 2
3     H=HH
      IS(1)=2
      IF(IS(2).NE.1) GO TO 22
      WRITE(6,20) (YE(I),I=1,N)
20    FORMAT(4X,"YE=",7E17.8)
      WRITE(6,21) H,K
21    FORMAT(3X,"H=",E17.8,"K=",I6)
22    CONTINUE
4     DO 5 I=1,N
5     YS(I)=YD(I)
      XS=XMU
      IF(H.GE.HMIN) GO TO 12
      IS(1)=4
      RETURN
12    IF(XMU+H.NE.XMU) GO TO 13
      IS(1)=5
      RETURN
13    CONTINUE
      CALL DSINT
      IF(IS(2).NE.1) GO TO 24
      WRITE(6,999) XMU,H
999   FORMAT(*X=*,E17.8,*DELTA=*,E17.8)
      WRITE(6,998) YMU(1)
998   FORMAT(*INTEGRAL=*,E17.8)
      WRITE(6,878) YH(1)
878   FORMAT(*ERROR=*,E17.8)

```

```

24 CONTINUE
DO 6 I=1,N
IF (ABS(YH(I)).GT.YE(I)) GO TO 7
6 CONTINUE
GO TO 9
7 H=0.5*H
K=2*K
DO 8 I=1,N
8 YD(I)=YS(I)
XMU=XS
GO TO 11
9 K=K-1
K2=K/2
IF (K.NE.K2*2) GO TO 11
DO 10 I=1,N
IF (ABS(YH(I)).GE.YEI*YE(I)) GO TO 11
10 CONTINUE
H=2.*H
K=K/2
11 HH=H
IF (K.LE.0) IS(1)=3
RETURN
END
SUBROUTINE USINT
COMMON/T/IS(2),YE(1),XMU,YMU(1),YH(1),YG(1),YD(1),YS(1),N,YEI,HS,
+HM1N,H,ZETA1,ZETA2,PI,IT,DE,ERR1,AA
DOUBLE YS,YD
THD=H*1./3.
DO 1 J=1,N
1 YMU(J)=YD(J)
XX=XMU
CALL YGRD
DO 2 J=1,N
YG(J)=THD*YG(J)
YH(J)=YG(J)
YMU(J)=YD(J)+YG(J)
2 YD(J)=YD(J)+0.5*YG(J)
XMU=XX+THD
CALL YGRD
DO 3 J=1,N
YG(J)=THD*YG(J)
3 YMU(J)=YD(J)+0.5*YG(J)
CALL YGRD
DO 4 J=1,N
YG(J)=THD*YG(J)
YMU(J)=YD(J)-0.125*YH(J)+1.125*YG(J)
4 YH(J)=YH(J)-4.5*YG(J)
XMU=XX+0.5*H
CALL YGRD
DO 5 J=1,N
YG(J)=THD*YG(J)
YMU(J)=YD(J)+YH(J)+6.0*YG(J)
YH(J)=YH(J)+4.0*YG(J)
5 YD(J)=YD(J)+2.0*YG(J)
XMU=XX+H
CALL TGRD
DO 6 J=1,N
YG(J)=0.5*THD*YG(J)
YD(J)=YD(J)+YG(J)
YH(J)=0.2*(YH(J)-YG(J))
6 YMU(J)=YD(J)
RETURN
END
SUBROUTINE YGRD
COMMON/T/IS(2),YE(1),XMU,YMU(1),YH(1),YG(1),YD(1),YS(1),N,YEI,HS,
+HM1N,H,ZETA1,ZETA2,PI,IT,DE,ERR1,AA
DOUBLE YS,YD
DIMENSION A(400),B(400)
UA1=1.
UA2=UA1
R1=1.
R2=R1
DO 20 J=1,400
A(J)=0.
20 B(J)=0.
IIN=1
PSI=0.
DPSI=0.
2 DO 10 I=IIN,IT
AM=I-1
H1=AM*(AM+1.)/(2.*AM+1.)
H2=AM-0.5
H3=AM+1.5
H4=2./(2.*AM+1.)
H5=AM+0.5

```

```

      F1=AA**2*UA1*H1*(EXP(-H2*ABS(ZETA1))-EXP(-H3*ABS(ZETA1)))/(SQRT(2.
+)*SINH(ABS(ZETA1)))
      F2=AA**2*UA2*H1*(EXP(-H2*ABS(ZETA2))-EXP(-H3*ABS(ZETA2)))/(SQRT(2.
+)*SINH(ABS(ZETA2)))
      A(I)=(F1/SINH(H5*ZETA1)-F2/SINH(H5*ZETA2))/(COTH(H5*ZETA1)-COTH(H5
+*ZETA2))
10  B(I)=F2/SINH(H5*ZETA2)-A(I)*COTH(H5*ZETA2)
      PRINT,(A(I),I=1,30),(B(I),I=1,30)
      DO 11 I=IIN+1,IT
      PSI=PSI
      UPSI=DPSI
      AM=I-1
      H1=AM*(AM+1.)/(2.*AM+1.)
      H2=AM-0.5
      H3=AM+1.5
      H4=2./(2.*AM+1.)
      H5=AM+0.5
      H6=(2.*AM+1.)/(AM+1.)
      H7=(2.*AM+3.)/(AM+1.)
      IF(I.LE.1) GO TO 777
      H8=(2.*AM-1.)/AM
      H9=(2.*AM+1.)/AM
777  IF(I.GT.2) GO TO 3
      IF(I.LE.1) GO TO 600
      VN=1.-0.5*(3.*XMU**2-1.)
      GO TO 5
600  VN=1.-XMU
      GO TO 5
      3  IF(I.GT.3) GO TO 199
      PNM=XMU
      PNO=0.5*(3.*XMU**2-1.)
199  PNP=(2.*AM+1.)*XMU*PNO/(AM+1.)-AM*PNM/(AM+1.)
      VN=PNM-PNP
      PNM=PNO
      PNO=PNP
      5  PSI=PSI1+(A(I)*COSH(H5*ZETA1)+B(I)*SINH(H5*ZETA1))*VN
      IF(I.GT.1) GO TO 697
      DPSI=DPSI+0.
      GO TO 11
697  DPSI=DPSI+0.5*H1*((H6*A(I)-H7*A(I+1))*SINH(H3*ZETA1)-(H8*A(I-1)
+-H9*A(I))*SINH(H2*ZETA1)+(H6*B(I)-H7*B(I+1))*COSH(H3*ZETA1)-(H
+8*B(I-1)-H9*B(I))*COSH(H2*ZETA1))*VN
      11 CONTINUE
      IF((ABS((PSI-PSI1)/PSI)).LE.ERR1).AND.(ABS((DPSI-DPSI1)/DPSI).LE.
+ERR1) GO TO 111
      IIN=IT+1
      IT=IT+5
      GO TO 2
111  CONTINUE
      IF((XMU.NE.1.).AND.(XMU.NE.-1.)) GO TO 1
      YG(1)=0.
      GO TO 15
      1  YG(1)=PI*DE*PSI*DPSI/(AA*(COSH(ZETA1)-XMU)*(1.-XMU**2))
15  RETURN
      END
      FUNCTION COTH(X)
      COTH=(EXP(X)+EXP(-X))/(EXP(X)-EXP(-X))
      RETURN
      ENO

```

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LIST OF SYMBOLS

The following is a list of some of the most important symbols used throughout this work.

a	radius of sphere, cm
A	Hamaker constant or effective Hamaker constant, ergs
A_{ijk}	Hamaker constant for interaction of media i and k through medium j , ergs
c	constant of bipolar coordinates
C	distance between the centres of two spheres (in Chapter 3), cm
C	concentration of the particles at time = t , g cm^{-3}
C_0	concentration of the particles at time = 0, g cm^{-3}
C_∞	concentration of the particles far from the collector
C_f	correction factor to van der Waals forces for retardation
d_b	bubble diameter, cm
$\bar{d}_{gv}$	particle geometric volume mean diameter, cm
d_p	particle diameter, cm
D_∞	diffusion coefficient far from the collector, $\text{cm}^2 \text{sec}^{-1}$
E	collection efficiency
E_a	adhesion efficiency
E_c	collision efficiency
F_A	attraction force, dynes
F_{mol}	sum of attractive and repulsive forces, dynes
F_R	repulsion force, dynes
H	surface separation between two spheres
H_0	minimum surface separation between two spheres
k	flotation rate constant, min^{-1}
K	parameter in the expression for virtual mass (in Sections 3.4, 3.5 of Chapter 3)

K	Boltzmann's constant, ergs $^{\circ}\text{K}^{-1}$
M	mass of a sphere
M'	mass of the liquid displaced by a sphere
N	number of particles per cm^3 at time = t
N_0	number of particles per cm^3 at time = 0
Pe	peclet number = $2r_b U/D_{\infty}$
q_i	number of atoms per cm^3 for medium i
Q	volumetric gas flowrate, $\text{cm}^3 \text{ min}^{-1}$
r	centre to centre distance between two spheres (Figure 3.9)
r_b	bubble radius, cm
r_c	collector radius, cm
r_p	particle radius, cm
R	r/R_1
R_1	bubble radius (in Sections 3.4, 3.5 of Chapter 3), cm
R_2	particle radius (in Sections 3.4, 3.5 of Chapter 3), cm
R_a	r_c/r_p
RA	R_2/R_1
R_b	bubble radius, cm
Re	Reynolds number = $2r_b \rho_f U_b / \mu$
S	distance between the surfaces of two spheres, cm
Sh	Sherwood number = $\frac{1}{4} E \text{ Pe}$
t	time
t	$\cos \eta$ (in Section 3.2.2 of Chapter 3)
T	absolute temperature, $^{\circ}\text{K}$
T	kinetic energy (in Section 3.4.1 of Chapter 3)
u_a	velocity of a sphere along the line of centres of two spheres, cm sec^{-1}
u_i	velocity of sphere i in y direction (in Section 3.4), cm sec^{-1}
u_p	velocity of a sphere perpendicular to the line of centres of two spheres, cm sec^{-1}

u_E	particle electromobility, $\mu\text{m/sec/V/cm}$
U, U_b	bubble terminal velocity, cm sec^{-1}
v_i	velocity of sphere i in x direction (in Section 3.4), cm sec^{-1}
V_A	attraction potential between two spheres, ergs
V_C	effective volume of flotation cell, cm^3
V_P	attraction potential between an atom and a sphere
V_R	repulsion potential between two spheres, ergs
V_T	total attraction and repulsion potential, ergs
x_∞, y_∞	position of centre of a particle far from a bubble
X_∞	x_∞/R_1
Y_∞	y_∞/R_1

GREEK SYMBOLS

α	parameter defining a sphere in bipolar coordinates for $\xi > 0$
β	parameter defining a sphere in bipolar coordinates for $\xi < 0$
ϵ	dielectric constant
ζ	zeta potential, mV
κ	reciprocal double layer thickness, cm^{-1}
λ	correction factor to Stokes drag term on a sphere
λ_a	correction factor for motion along the line of centres of two spheres
λ_c	characteristic wavelength, cm
λ_{ij}	London constant for interaction of atom i with atom j
λ_p	correction factor for motion perpendicular to the line of centres of two spheres
μ	dynamic viscosity, poise
μ	$\cos \eta$ (in Sections 3.2.1, 3.4.1, Chapter 3)
ν	kinematic viscosity
ρ_b	bubble density, g cm^{-3}
ρ_f	fluid density, g cm^{-3}
ρ_i	density of sphere i, g cm^{-3}
σ	surface charge density
τ	time (in Sections 3.4, 3.5, Chapter 3)
τ	κr_p
ϕ	potential function
ψ	stream function
ψ	surface potential (in Section 3.3, Chapter 3)

(ξ, η, ϕ) bipolar coordinates

(z, ρ, ϕ) cylindrical coordinates