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THE EFFICIENCY OF PARTICLE REMOVAL

BY

DISSOLVED AIR FLOTATION

by

ANURAK PETIRAKSAKUL

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of the Degree of Doctor of Philosophy

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Abstract

The efficiency of flotation processes may be improved through an understanding of the flotation models. Two mathematical models, particle trajectory and mixing zone models, have been modified and used to describe flotation results obtained from a semi-continuous flotation rig. Two types of clay suspensions, kaolin and Wyoming bentonite, were used as representative raw materials treated with a cationic surfactant, hexadecyltrimethylammonium bromide (HTAB), and/or coagulants i.e. alum, ferric chloride and polyaluminium chloride (PAC). HTAB concentrations were varied in the range of 1×10^{-6} to 3×10^{-5} mol/L. Alum at a concentration of 40 mg/L, ferric chloride at 40 mg/L and PAC at 10 mg/L were the selected coagulant dosages to be used in flotation tests. For the clay-HTAB-coagulant system, a HTAB concentration of 1×10^{-5} mol/L was used in the flotation tests. Suspension flow rate was chosen at 2 L/min and recycle ratios were varied in the range of 6-40% at room temperature. Two categories, suspensions with and without flocs, have been considered.

The trajectory model gave a good match even taking account of the decreases in flotation efficiency at high recycle ratios where flocs had been broken by shear gradients. This model included hydrodynamic and surface forces i.e. electrostatic, van der Waals and hydrophobic forces and was calculated by a Runge Kutta technique. The effect of the shear force on a size reduction was determined from particle size measurements (Lasentec apparatus) in a mixing tank and the results showed a decrease of floc sizes with increasing agitator speeds. Bubble zeta potentials obtained using a modified rectangular cell in a Rank Brothers' apparatus gave points of zero charge at concentrations of 1.61 x 10⁻⁹ mol/L for HTAB, 1.69 x 10⁻⁸ mol/L for tetradecyltrimethylammonium (TTAB) and 2.37 x 10⁻⁷ mol/L for dodecyltrimethylammonium bromide (DTAB) at 25°C respectively. Van der Waals and hydrophobic or hydration forces were obtained from contact angle measurements on solid surfaces. The hydrophobic forces were increased by increasing HTAB concentrations while the hydration effects occurred upon the addition of coagulants to the suspensions. A flocculation model using the extended-DLVO theory showed a good correlation when compared to experimental results.

For the mixing zone model, an attachment efficiency for the aggregation of a particle and a bubble was proposed from a ratio between the energy barrier (E_1) and the maximum free energy at equilibrium. When particle size is constant, the attachment efficiency values rise with increasing hydrophobic force levels. On the other hand, when floc sizes are increased, the attachment efficiencies are decreased due to the increase in the repulsive long range van der Waals force. Keywords : dissolved air flotation, water, clays, bubbles, surfactants, zeta potential, hydrophobic force, floc break up, mathematical model, contact angle, attachment efficiency.

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Nomenclature

A	:	area of an element of liquid volume under the influence of an electric field	[m ²]
A_1	:	empirical constant which is a function of the Reynolds	[-]
1		number of the bubble	
A_{h}	:	projected area of a bubble	$[m^2]$
A_c	:	cross sectional area of rectangular cell = $l_c x d_c$	$[cm^2]$
A_d	:	amount of dissolved air	[mg/L]
A'_d	:	amount of air released in a flotation cell	[mg/L]
A_{H}	:	effective Hamaker constant between the bubble and particle	[J]
A_i	:	interfacial area	[m ²]
A_s	:	air to solid ratio	[-]
A_{ii}	:	Hamaker constants of substance <i>i</i>	[1]
A_{iii}	:	Hamaker constants of substance <i>i</i> in medium <i>j</i>	[ກ]
A_{iik}	:	Hamaker constants of substances i and k in medium j	[1]
a	:	particle radius	[m]
a_c	:	chemical activity	[-]
a_1	:	coefficient	[-]
C	:	concentration of electrolyte or surfactant	[mol/L]
C_0	:	concentration of electrolyte or surfactant at zero charge	[mol/L]
C_{1}, C_{2}	:	exponential constants in hydrophobic force	[N/m]
C_B	:	solution concentration	[mol/L]
C_D	:	drag coefficient	[-]
C_i	:	concentration of ions per unit volume	[mol/L]
C_{S}	:	floc strength coefficient	[-]
с	:	concentration of air in the saturated water	[mg/L]
C _s	:	solid concentrations in suspension	[mg/L]
D^{+}	:	dielectric constant	[-]
D_{1}, D_{2}	:	decay lengths	[m]
D_T	:	flocculator diameter	[m]
d	:	distance for two plates	[m]
d_b	:	bubble diameter	[m]
d_c	:	internal path length	[cm]
df	:	floc diameter	[m]
d_p	:	particle diameter	[m]
d_s	:	mean stable floc size	[m]
d_{fd}	:	bubble-floc agglomerate diameter	[m]
J			

d _{col}	:	column diameter	[m]
d _{noz}	:	nozzle diameter	[m]
E_1	:	energy barrier at H_1	[J]
E_2	:	energy barrier at H_2	[J]
E _c	:	collection efficiency defined as the fraction of particles in the	[-]
		path of the bubble which actually coalesce with it and removed	
		from the cell	
E_k	:	kinetic energy	[1]
E'	:	kinetic energy of detachment	[J]
E_{Z}	:	field strength	[V/cm]
ΔE	:	sedimentation potential	[mV]
е	:	elementary electric charge = 1.6021×10^{-19}	[C]
F_D	:	drag force	[N]
F _e	:	electrostatic force acting between the bubble and the particle	[N]
F_h	:	normal component of hydrodynamic force acting on the particle	[N]
F_n	:	total force acting on the particle normal to the bubble surface	[N]
F_{ν}	:	van der waals force acting between the bubble and the particle	[N]
F_t	:	total force	[N]
f	:	efficiency of dissolved-air releasing in flotation cell	[-]
f_1, f_2, f	3:	correction factors characterising the short range effect	[-]
		hydrodynamic interaction	_)
G	:	velocity gradient	[s ⁻ ']
ΔG_{SL}	:	free energy of the solid-liquid interface	[mJ/m ²]
ΔG_{SL}^{LW}	:	apolar free energy of the solid-liquid interface	[mJ/m ²]
ΔG_{SL}^{AB}	:	polar free energy of the solid-liquid interface.	[mJ/m ²]
ΔG_{131}^{LW}	:	apolar free energy of the solid 1 and in liquid 3	[mJ/m ²]
ΔG_{131}^{AB}	:	polar free energy of the solid 1 in liquid 3	[mJ/m ²]
ΔG_{132}^{LW}	:	apolar free energy of the solids 1 and 3 in liquid 2	[mJ/m ²]
ΔG_{132}^{AB}	:	polar free energy of the solids 1 and 3 in liquid 2	[mJ/m ²]
g	:	gravitational constant	[m/s ²]
Η	:	ratio of h_1/r_p	[-]
H_L	:	height of the liquid column in sedimentation potential test	[m]
H_t	:	particle height in a column	[m]
ΔH	:	increment of the liquid column high in sedimentation potential	[m]
		test	
h	:	distance between particles measure between surfaces	[m]
h_{1}, h_{2}	:	distance between particles at E_1 and E_2	[m]

Ι	:	current	[mA]
Is	:	streaming current	[mA]
I _{st}	:	streaming current at stationary level	[mA]
K	:	Henry constant	[kPa/mgL ⁻¹]
K _A	:	aggregation constant	[-]
K _B	:	floc breakup coefficient	[-]
K _h	:	hydrophobic force constant	[Nm ⁻¹]
K _s	:	specific conductivity	[ohms ⁻¹ cm ⁻¹]
k _i	:	flotation rate constant	[s ⁻¹]
k _{B.}	:	Boltzmann constant, = 1.38×10^{-23}	[J/K]
k _G	:	collision rate coefficient related to gravitational motion	[s ⁻¹]
k _p	:	collection kinetic constant	[s ⁻¹]
k_T	:	collision rate coefficient related to turbulent fluid motion	[s ⁻¹]
L	:	distance between electrodes with which the sedimentation	[m]
		potential was measured	
L_T	:	flocculator height	[cm]
L _{MZ}	:	mixing zone length	[m]
l	:	effective inter electrode distance	[cm]
l	:	distance between two semi-infinite flat parallel bodies	[m]
lB	:	exponent for floc strength test	[-]
l _c	:	internal cell height	[cm]
l_L	:	limiting trajectory	[m]
М	:	mass flow rate	[kg/s]
N_A	:	Avogadro number = 6.0225×10^{23}	[1/mol]
N _b	:	number of bubbles per unit volume	[1/m ³]
N _p	:	number of particles per unit volume	[1/m ³]
N_{p0}	:	initial number of particles per unit volume	[1/m ³]
N_t	:	total number of particles in the flotation cell	[-]
n	:	number of particles	[-]
<i>n</i> ₀	:	bulk concentration of each ion	[mol/L]
n ₊ , n ₋	:	respective number of positive and negative ions per unit	[-]
		volume at points where the potential is φ	
n _c	:	number of carbon atoms	[-]
n _p	:	power index constant normally, $n = 2$ for the bubbles used in flo	tation
n_v	:	number of particles per unit volume	$[1/m^3]$
n_i^{σ}	:	amount of component <i>i</i> in the surface phase σ	[mole]
Р	:	absolute pressure	[Pa]
P_J	:	jet power	[W]

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u _B	: bubble rise velocity	[m/s]
u_p	: velocity of particle	[m/s]
u _n	: normal component of the fluid velocity	[m/s]
uα	: tangential velocity of fluid	[m/s]
u _{np}	: velocity of particle in normal direction	[m/s]
$u_{\alpha p}$: velocity of particle in tangential direction	[m/s]
u _{noz}	: nozzle velocity	[m/s]
V	: volume of the medium	[m ³]
VA	: attractive London-van der Waals (dispersion) energy	y [J]
V_E	: repulsive electrostatic interaction energy	[J]
V _c	: total volume of the flotation cell	[m ³]
V_f	: volumetric concentration of the aggregates	[m ³]
V _m	: molar volume of the medium	[m ³ /mol]
V_p	: volume of colloidal particles per unit volume of sus	pension [-]
V _s	: structural or hydration energy	[J]
V _T	: total volume of the medium	[m ³]
V_t	: net interaction energy	[J]
V _{MZ}	: volume of the mixing zone	[m ³]
V_{col}	: volume of flotation column	[m ³]
ΔV	: total volume of particles included in the medium	[m ³]
v	: velocity of liquid	[m/s]
v _p	: paddle mean velocity	[m/s]
v_Z	: velocity of liquid at any x in z-direction	[m/s]
veo	: maximum velocity of liquid at some distance from t	the wall in [m/s]
	z-direction	
W_a	: sum of the work of adhesion	[J]
$W_{\delta s}$: transfer energy to bring the ion from the bulk of solu	ution up [J/mole]
	to the plane δ_s	
W ₁₃₂	: maximum free energy per unit area at equilibrium	[mJ/m ²]
x	: distance from a surface	[m]
x_r	: ratio of r/r_b	[-]
Ż	: ion valency of electrolyte	[-]

Greek letters

α	: angle between a particle and bubble	[radian]
θ	: contact angle	[degree]

P_{OT}	: flocculator power	[W]
P_R	: collection probability	[-]
P _{ca}	: capillary pressure	[Pa]
P _{in}	: power input	[W]
P _{hy}	: hydrostatic pressure	[Pa]
\overline{P}	: mean collision-agglomeration factor	[-]
ΔP	: pressure gradient in streaming potential test	[Pa-s]
\mathcal{Q}	: charge	[C]
Q_g	: flow rate of gas in the flotation cell	[m ³ /s]
Q_M	: volumetric flow rate of air	[L/s]
Q_{v}	: volumetric flowrate of suspension	[L/s]
R	: ratio of r_p/r_B	[-]
Re	: Reynolds number of the bubble	[-]
R _o	: recycle flow rate	[L/min]
R _c	: column radius	[m]
R _g	: gas constant = 8.314	[J/mol-K]
R _s	: resistance = V/I	[Ω]
R_t	: capillary diameter	[m]
r	: distance from a centre (cylindrical coordinate, Chapter 3)	[m]
r	$: r_b + h_I + r_p$	[m]
<i>r</i> ₁₁	: interatomic distance in the particle $(6\pi r_{11}^2 = 1.44 \times 10^{-18} \text{ m}^2)$	[m]
r _b	: bubble radius	[m]
r _c	: critical radius	[m]
r_p	: particle radius	[m]
$r_{\delta s}$: radius of the adsorbed ion at the plane δ_s	[m]
S	: cross-sectional area of the liquid column	[m ²]
S_c	: contactable area	[m ²]
S_T	: total entropy	[J/K]
S_{wt}	: weight of solid inflow	[mg/s]
S	: distance from inside face to stationary level	[cm]
Т	: temperature	[K]
t	: time	[s]
U	: total energy of a system	[J]
U_B	: electromobility of bubble [µms	s ⁻¹ /Vcm ⁻¹]
U_E	: electromobility of particle [µms	s ⁻¹ /Vcm ⁻¹]
U _{em}	: electromobility [µms	s ⁻¹ /Vcm ⁻¹]
U^{σ}	: thermodynamic energy of a surface phase σ	[J]
u	: uniform fluid velocity relative to the bubble	[m/s]

δ	: distance from plate wall to plane of shear	[m]
3	: permittivity	[F/m]
0 ³	: permittivity at free space = 8.854×10^{-12}	[F/m]
κ	: Debye-Huckel parameter	[cm ⁻¹]
<i>f(</i> к <i>a</i>)	: Debye-Huckel function	[-]
ΥL	: surface tension in solution	[Pa]
γο	: surface tension of free solute solution	[Pa]
γ _{lv}	: surface tension of liquid-air interface	[mJ/m ²]
γ ^{LW} γi	: apolar surface energy of substance <i>i</i>	[mJ/m ²]
γ _i	: negative polar surface energy of substance <i>i</i>	[mJ/m ²]
γ;+	: positive polar surface energy of substance <i>i</i>	[mJ/m ²]
γ <i>ΤΟΤ</i>	: total surface energy of substance <i>i</i>	[mJ/m ²]
λ	: specific conductance	$[\Omega^{-1} \mathrm{cm}^{-1}]$
μ _i	: chemical potential of component i	[J/mole]
μ	: viscosity	[Pa-S]
η _a	: attachment efficiency	[-]
η_c	: collision efficiency	[-]
η _d	: Brownian diffusion efficiency	[-]
η_{da}	: detachment efficiency	[-]
η _i	: interception efficiency	[-]
η _g	: efficiency of the gravity forces	[-]
η τ	: total single-collector collision efficiency	[-]
η <i>τ</i>	: efficiency of drag forces	[-]
η _{Τc}	: particle capture efficiency per bubble	[-]
Ψ	: stream function	[-]
φ	; potential	[V]
φ₀	: Nernst potential or surface potential	[V]
φ _d	: Stern potential	[V]
ϕ_{δ^x}	: potential at plane δ_s	[V]
ϕ_{sh}	: sphericity of bubble-floc agglomerate	[-]
Φ	: bubble volume concentration	[1/m ³]
φ ′	: van der Waals energy per CH_2 group in unit of $k_B T$	
¢	: van der Waals energy	[J]
ρ	: volume charge density = $\sum_{i} n_i z_i e$	
ρ _m	: density of the medium.	[kg/m ³]

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ρ _p	:	particle density	[kg/m ³]					
ρ _w	:	water density	[kg/m ³]					
Γ_i	:	surface excess concentration of component <i>i</i>	$[mol/m^2]$					
Γ_{δ}^{+}	:	surface excess concentration or adsorption density	[mol/m ²]					
$(\Gamma^+_{\delta})_0$:	adsorption density of carbons at plane δ at zero charge	[mol/m ²]					
$\Gamma^{S/L}$:	adsorption density at the solid-liquid interface	[mol/m ²]					
σ_0	:	charge density at a surface	[C/m ²]					
σ_{m}	:	surface charge density corresponding to a monolayer of counter-	[C/m ²]					
		ions						
σ	:	phase	[-]					
σ,	:	charge density of the diffuse region of the double layer	[C/m ²]					
τ	:	retention time	[s]					
ζ	:	zeta-potential	[mV]					
DAF	:	Dissolved air flotation						
DTAB	:	dodecyltrimethylammonium bromide, C ₁₅ H ₃₄ NBr (MW 308.3)						
HTAB	:	hexadecyltrimethylammonium bromide or CTAB, Cetyltrimethy	1-					
		ammonium bromide, C ₁₉ H ₄₂ NBr (MW 364.5)						
KL	:	kaolin						
PAC	:	Polyaluminium chloride						
SDS	:	sodium dodecyl sulphate, C ₁₂ H ₂₅ O ₄ SNa (MW 288.4)						
TTAB	:	tetradecyl-trimethylammonium bromide, C ₁₇ H ₃₈ NBr (MW 336.4)						
WRC	:	Water Research Centre						
WB	:	Wyoming bentonite						

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Chapter 1

Introduction

1.1 Introduction

Water is an important substance in all lives. Approximately, two-third of the Earth's surface is covered by water. However, nearly 97% is seawater and the remaining 3% is freshwater [1]. In the UK, the estimated total public water supply in 1990 was 20,100 Ml/d, which was obtained from upland surface water, lowland surface water and groundwater. From the National Comparability Study prepared by the Water Research centre (WRC) for 1985/1986, the average raw water quality is shown in Table 1.1. Lowland water gives higher values of turbidity than either groundwater or upland surface water. River waters have coliform concentrations higher than reservoir surface water and groundwater.

parameter	upland	upland	ground-	lowland	lowland
	reservoir	river	water	reservoir	river
Colour ([°] H)	36.4	22.9	5.5	11.9	23.6
Turbidity (NTU)	2.9	2.7	2.2	3.6	7.0
Mn (mg/L)	0.091	0.029	0.034	0.053	0.064
Fe (mg/L)	0.33	0.18	0.28	0.17	0.42
Hardness (mg CaCo ₃ /L)	35.6	50.9	291.5	208.8	146.0
pН	6.65	6.65	7.17	8.0	7.66
Coliforms (No./100ml)	72.2	721.0	38.5	281.1	2.2×10^4

Table 1.1 Average raw water quality from different source types in the UK [2].

1

It is of great importance for water quality control to be undertaken by each government. Unfortunately, quality standards of drinking, domestic and waste water vary from country to country according to the differences in national resources. However, there are guideline values, for example, from the World Health Organisation (WHO) and European Community which can be applied. In the UK, the legal requirements for water quality were defined by the Water Act 1989, which was combined with European Community standards for drinking water [2].

Some examples of water treatment processes are shown in Figure 1.1. The principal requirements for drinking water are that it should be clear of pathogens and toxic chemicals. The step of disinfection is very important in the preparation of drinking water. Chlorination is the most commonly used method to deal with micro-organisms. The early results showed that the efficiency of disinfection decreased with increasing turbidity since chlorine can react with suspended matters. Turbidity is caused by the presence of suspended solids such as clay, decaying vegetation and algae. The removal of turbidity can be achieved by either ultra-filtration or slow sand filtration following a separation process such as sedimentation or flotation.

Flotation is a separation process found in primary treatment, which is used for the removal of suspended solids, oils and fat from liquid streams. This process is not only used in clarification [3] but also in mineral recovery [4-6], sludge thickening [7] and wastewater treatment [8-10]. In England and Wales, flotation and sedimentation are commonly used in the clarification steps of water treatment processes [2].

The flotation process is considered to have a complicated mechanism due to the interaction between the three phases in the process. This is governed not only by the effects of the surface forces but also by the hydrodynamic interactions around the rising bubbles in the liquid phase. Thus, the efficiency of flotation units may be

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improved through an understanding of surface chemistry and the capture mechanisms between particles and bubbles.



Figure 1.1 Examples of water treatment processes (DAF is Dissolved Air Flotation and FBC is Floc Blanket Clarification).
An overview diagram for this study is shown in Figure. 1.2. A major objective of this thesis will be to determine the surface forces, namely electrostatic, van der Waals and hydrophobic forces. The electrostatic forces between particulate surfaces are studied in terms of the zeta potentials of bubbles and particles. Meanwhile, the van der Waals and hydrophobic forces are represented by both the surface tension and contact angle in the three-phase system. The flotation models will be described by using experimental measurements of surface forces including floc strength and hydrodynamic data. Finally, a comparison between the flotation models and the experimental results obtained from a DAF operated in semi-batch pilot-scale will be undertaken using kaolin and Wyoming bentonite suspensions treated with chemicals.



Figure 1.2 Overview diagram of this work.

1.2 Objectives

- 1. To study the characteristics of the van der Waals forces, hydrophobic forces and electrostatic forces found on both bubble and particle surfaces.
- To develop a capture model involving shear effects, surface forces and the hydrodynamics of bubbles and particles.

3. To determine the efficiency of the separation of clay-water suspensions using dissolved-air flotation.

1.3 Scope

- 1. Measure zeta potentials as follows:
 - a) the zeta potentials of bubbles in aqueous solutions of cationic surfactants.
 - b) the zeta potentials of clay particles in either surfactant or coagulant solutions.
- 2. Measure contact angles between clays and solutions to determine Hamaker constants and hydrophobic and/or hydration free energies.
- 3. Measure particle and floc sizes in a variety of shear gradients in a stirred tank to represent the strength of flocs.
- 4. Develop a new theoretical model for the removal of clay particles, with and without agglomeration, by fine bubbles.
- 5. Find the optimum conditions for the coagulation of clays by varying chemical dosages.
- 6. Measure separation efficiencies for the semi-continuous DAF by varying the recycle ratio, chemical dosages and cationic surfactant concentrations.
- 7. Compare the results obtained from the experiments and the model.

1.4 Benefits

- 1. Knowledge of the relationship between the zeta potentials of both bubble and clay particles and the chemical concentrations used in water treatment.
- 2. Knowledge of the relationship between contact angles and surface free energy.
- 3. Identification of controlling parameters in the dissolved-air flotation process.
- 4. The availability of a mathematical model to predict removal efficiencies.
- 5. The provision of experimental data for scale up.

Chapter 2

Literature review

2.1 Introduction

The electrical surface charge or zeta potential is the potential between the shear surface of the particulates, both the gas bubbles and the solid particles, and the bulk solution. Zeta potentials can be obtained by using electrokinetic theory as explained in some detail in Chapter 3. This chapter will focus on the measurements of the zeta potential of gas bubbles to investigate the effects of pH and the presence of salts and surfactants, such as sodium sulphate, sodium dodecyl sulphate, etc. In coagulation and flocculation processes, pH changes, coagulant types and dosages are reflected by the zeta potential and affect the removal efficiency of clay suspensions. Finally, flotation processes will be reviewed in terms of the operating conditions for water treatment.

2.2 Bubble studies

2.2.1 Zeta potentials

According to Okada and Akagi [11], the measurement of the zeta potential of gas bubbles was described in 1861 by Quincke who was the first person to report a study of the surface charge of bubbles. He found that the air bubble moved to the anode in water when a direct current was applied to electrodes in a capillary tube. In addition, there were several workers, such as Brandon and co-workers [12], Collins and coworkers [13, 14], Kubota and co-workers [15] and Okada and co-workers [11, 16, 17] who studied the surface charges of bubbles using different techniques, each based on an electrokinetic effect.

Electrokinetic phenomena can be classified into four distinct effects according to the way in which motion is induced, namely, electro-osmosis, electrophoresis, streaming

potential and sedimentation potential [18]. All of these electrokinetic techniques can be used to measure the zeta potential of solid particles and gas bubbles. However, zeta potential measurements of gas bubbles by the early workers generally used the electrophoresis method and few workers used the sedimentation potential (or the Dorn effect) [15, 19, 20] and the streaming potential [21] techniques as shown in Figure 2.1. Electrophoresis is a phenomenon in which the particles move in a continuous stationary liquid by application of an electric field. On the other hand, the sedimentation potential effect is shown when a charged particle is allowed to move through the liquid. Streaming potential is evident when an electric current is generated as the liquid in a capillary tube is moved by an applied pressure gradient [18]. The electrophoresis technique is used because the zeta potential measurement of gas bubbles by this method seems to be the most convenient experiment while the streaming potential technique is not sufficiently well understood to obtain meaningful information.

Thus, the electrophoresis technique is the accepted method for obtaining zeta potential measurements of gas bubbles. There are three methods of making the electrophoretic mobility measurements, using a modified rectangular cell, a spinning cylinder [26] or a plane-shear method [27]. The rectangular cell is used extensively for studying the surface charge of bubbles by applying a gas such as oxygen, hydrogen, chlorine, air or nitrogen. Early workers used electrolytic cells to produce oxygen, hydrogen and chlorine bubbles in modified rectangular cells [14, 15, 22, 23]. Later studies used the air and nitrogen bubbles generated by reducing the pressure of gas-saturated solutions at high pressure, e.g. 0.5 MPa, to atmospheric pressure [11, 16, 17, 24, 25] before flowing the solution into the cell.

The spinning cylinder technique is a method in which the bubble moves along the axis of a horizontal spinning cylinder during an applied electric field. This experiment is easy to set up but it is difficult to calculate the zeta potential of bubbles from data because the mobility needs to be known at a stationary level.

7



Figure 2.1 The several techniques for zeta potential measurement of gas bubbles.

zeta potential of N₂ bubbles with a rectangular cell $(0.83 \times 23 \times 73 \text{ mm})$.

The plane-shear method is a technique which determines the electromobility at the airsolution interface in an open quartz cell. It seems that this method takes a long time for each experiment and vibration of the solution surface needs to be avoided during measurements under a microscope [27].

Methods for determining the zeta potentials of bubbles have been studied since the nineteenth century. However, the most interesting papers were published in the 1970s. The pioneering works used electrolytic cells to produce the bubbles and later workers used dissolved-gas bubbles.

Collins and co-workers [14] studied the measurement of the charge on small oxygen gas bubbles at 25°C. The bubbles were generated in a solution saturated with oxygen produced by electrolysis in an electrophoretic cell (Rank Brothers apparatus with quartz cell 1 x 10 x 40 mm). The cell was modified by drilling two small holes and sealing with platinum wires. The 12 V potential was applied to the bottom wire connected to the earth so that the bubbles were not charged by the circuit. When generated bubbles moved vertically across a stationary level, the zeta potential was obtained by noting the horizontal velocity of the bubbles under the applied electric field and calculated by using Smoluchowski's equation. This work used an upper micrometer, moved up and down, keeping the bubble in the field of view for a sufficient time to measure its horizontal velocity. Thus, bubbles of diameter greater than 35 μ m could not be followed by this technique because they rose too quickly. However, this problem was solved by Fukui and Yuu [22] who also determined the electromobility of small oxygen gas bubbles but they used a video recording system and a different quartz cell 1.1 x 23 x 73 mm in which Mori and co-workers [28] claimed that the effect of a shorter side wall could be neglected. However, it seems that the results from the different cell were slightly affected because the zeta potentials measured by Fukui and Yuu show approximately 10% difference when compared to the Collins' report [14]. Collins and co-workers claimed that there was a systematic error of up to 8% during observations in the region 0.15 cm above and below the cell midpoint because the planes in which the bubbles rise were not the same as those of the stationary levels. This was also supported by Okada and Akagi [11] who measured the zeta potentials of air bubbles by using a quartz cell 0.972 x 23 x 73 mm and they claimed that their results agree well with Collins' work.

The electrophoretic mobility of small air bubbles which were generated using the dissolved air technique was investigated by other researchers such as Kubota and coworkers [15], Yoon and Yordan [24] and Okada and Akagi [11]. Kubota and coworkers used the air saturated solution withdrawn from a pressure vessel where it had been held at 0.5 MPa for 1 hour. After filling the solution into the conventional rectangular cell, internal dimensions 1.04 x 22.4 x 70 mm, the bubble motion was measured at a stationary level and electromobility calculated by using Smoluchowski's equation. It seems that this method was successful when surfactants were added to a pressure vessel in order to create stable bubbles. Yoon and Yordan [24] also determined the zeta potential of bubbles by using the modified rectangular cell in a microelectrophoresis apparatus (Rank Brothers Mark II). Two pieces of glass tubing (internal diameter 1.6 mm) were fitted to the cylindrical parts of the cell. The bubble-suspension solution, generated by reducing the pressure of a saturated solution to atmospheric pressure, was passed through the cell by a pump. The flow of the bubble suspension was stopped when the mobilities were measured at two stationary levels. On the other hand, Okada and Akagi [11] developed a technique for the measurement of the zeta potential of bubbles by using the modified rectangular quartz cell, 0.972 x 23 x 73 mm, in the microelectrophoresis apparatus. The cell was modified by fitting a nozzle, diameter 1 mm, in the bottom and a capillary glass tube on the top. The bubbles were generated by dissolving air into a solution at high pressure, 0.5 MPa, and kept for approximately one hour. When the pressure was released by opening the control valves, the bubble solution also flowed into the cell. The dissolved-air bubbles, 20-40 μ m, moved vertically across two stationary levels and their electromobilities were measured by noting the horizontal velocity of the bubbles during the applied electric field of between 2 and 5 V/cm, with a video

recording system. Both of the two last methods were successful in measuring the zeta potentials of air bubbles.

After Kubota and co-workers [15] succeeded in obtaining zeta potential measurements of air bubbles, the electrophoretic mobilities of small nitrogen gas bubbles were investigated using the dissolved-gas technique again. Kubota and Jameson [25] used a similar method to that described in previous work [15] but they used nitrogen gas instead of air. By using nitrogen gas, very small bubbles, less than 4 μ m, were nucleated at random times and places within the liquid. After filling the solution into the cell, the velocity of the nitrogen bubbles was measured at a stationary level and the electromobility was calculated by using Smoluchowski's equation.

In general, bubbles in cationic surfactants are produced with positive charges while the bubbles generated in anionic surfactants are negatively charged and nonionic surfactants, on the other hand, produce negatively charged bubbles in the alkaline pH range and positively charged bubbles in the acidic pH range. The results of the zeta potentials of bubbles were investigated in solutions containing both surfactants and coagulants. These can be summarised as follows:

Collins and co-workers [14] used test solutions each containing 5 x 10^{-5} mol/L of the cationic surfactant (cetyltrimethylammonium bromide, CTAB) and 0.5% (ν/ν) of ethanol with concentrations of sodium sulphate in the range between 5.0 x 10^{-4} and 10^{-2} mol/L. The results showed that the addition of sodium sulphate could decrease the zeta potential of bubbles from 63 mV to 50 mV because of the double layer reduction.

Brandon and co-workers [23] reported that all bubbles, in surfactant-free solutions, gave a point of zero charge at pH 2-3. The interesting results showed that the absolute values of electrophoretic mobility of bubbles increased linearly when bubble sizes were increased in a range of bubble diameters between 30 and 200 μ m. However,

these results contrasted with Usui and co-workers [20] who measured the zeta potential of argon gas bubbles by using the sedimentation potential method. They claimed that the absolute values of electrophoretic mobility of bubbles increased when bubble sizes were decreased in a range of bubble diameters between 200 and 1,400 µm. This will be discussed again in the next section. Moreover, Brandon and coworkers reported that the absolute values of the electromobility of bubbles adsorbed by surfactants rose exponentially when the concentrations of both anionic and cationic surfactants were increased. The bubble charges in the cationic surfactant solution, dodecyltrimethylammonium bromide, DTAB, at the pH 2.4 did not change the direction of electromobility but the electromobility of bubbles in the cationic surfactant solutions at the pH 6.9 and 10.5 turned the charges from positive to negative at concentrations of 4 x 10^{-6} and 8 x 10^{-6} mol/L, respectively. For anionic surfactant solutions using sodium dodecyl sulphate, the sign of the bubble charge at pH 2.4 was reversed from negative to positive in solutions of surfactant concentration of 2 x 10^{-7} mol/L. The anionic surfactant concentration at the bubble surface was 2.8 x 10^{-10} mol/m² and the surface charge density was $+27\mu$ C/m².

Kubota and co-workers [15] used test solutions containing three kinds of surfactant, two anionic types (sodium dodecyl sulphate and sodium dodecylbenzene sulfonate) and a cationic one (cetylpyridinium chloride), in a range of surfactant concentrations between 10^{-6} and 8 x 10^{-3} mol/L. It was shown that the negative potentials of bubbles in both anionic surfactants increased with increasing concentration of the surfactants. In addition, the dodecylbenzene sulfonate ion was more strongly adsorbed on the bubble surface than the dodecyl sulphate ion because the presence of further methylene groups leads to an increase in the surface excess. For cationic surfactants, the results showed that positive zeta potentials were observed and their values increased with increasing concentration of cationic surfactant. This effect might be due to the increase of the adsorption densities of cetylpyridinium ion on the bubble surface.

Yoon and Yordan [24] determined the zeta potential of bubbles of test solutions containing seven types of surfactant, two anionic (sodium dodecyl sulphate and sodium oleate), two cationic (dodecylamine hydrochloride and cetylpyridinium chloride) and three nonionic surfactants (polypropylene glycol, polyoxyethylene methyl ether and polyoxyethylene dodecyl ether) in the range of surfactant concentration between 10^{-5} and 10^{-2} mol/L. These results were similar to the work of Kubota and co-workers [15] with sodium dodecyl sulphate. However, the results of Yoon and Yordan's work showed that the magnitudes of the zeta potentials were reduced when the pH approached the p K_q value. On the other hand, the zeta potential of bubbles in two nonionic surfactants (polypropylene glycol and polyoxyethylene methyl ether) were negative in neutral and alkaline solutions and positive in acidic solutions. In another nonionic surfactant, polyoxyethylene dodecyl ether, the zeta potentials of bubbles were negative over the all of the pH range studied.

Okada and Akagi [11] used test solutions containing two types of surfactants. Sodium dodecyl sulphate, an anionic surfactant, was used at a concentration of 1×10^{-4} mol/L at 20° C, and NaCl, CaCl₂ and Al₂(SO₄)₃ electrolytes were added, respectively. CTAB, a cationic surfactant, was used at a concentration of 5×10^{-5} mol/L at 25° C. The results showed that the zeta potential of air bubbles in the absence of the electrolytes was strongly negative and the bubble zeta potentials in NaCl and CaCl₂ were negative but in Al₂(SO₄)₃ it was positive because of the specific adsorption of aluminium and hydrated aluminium ions on the surface of the bubble. However, their absolute potentials reduced when the concentrations of all electrolytes were increased. On the other hand, the zeta potential of bubbles in CTAB gave positive values and its potential decreased with increasing electrolyte concentration. This result agreed well with the measurements of the work of Collins and co-workers [14] made under the same conditions.

Kubota and Jameson [25] reported on test solutions each containing one of four electrolytes, NaCl, MgSO₄, $Al_2(SO_4)_3$ and $AlCl_3$, in the range of concentrations

between 10⁻⁷ and 10⁻² mol/L at pH 5.6 and 25°C. The absolute mobilities of bubbles in NaCl and MgSO₄ solutions were negative and decreased with increasing concentration of each electrolyte. However, the mobilities of bubbles in $Al_2(SO_4)_3$ and AlCl₃ solutions were negative at each concentration less than 10⁻⁶ mol/L, approximately. The value of the positive charge on the bubbles, obtained at the concentration of 10⁻⁶ mol/L in each aluminium-salt solution, tended to increase to the maximum with increasing concentration. For the mobility of bubbles measured in a pH range of 2-10, it was concluded that the negative potentials of bubbles in distilled water without an electrolyte increased with increasing pH in the range of the pH 3-9, adjusted by adding hydrochloric acid and sodium hydroxide solution, and tended to decrease at approximately pH 10 because of the increasing ionic strength of the However, the zeta potential at a very low pH was positive due to a solution. preferential accumulation of H⁺ ion. Moreover, this work showed the results of the mobilities of bubbles in five types of cationic surfactants: dodecylammonium chloride (DACL), n-decyltrimethylammonium bromide, n-dodecyltrimethylammonium bromide, n-tetradecyltrimethylammonium bromide, and n-hexadecyltrimethylammonium bromide, HTAB or CTAB. For the DACL solution, the bubbles were negatively charged at a low concentration showing an isoelectric point at a concentration of 10^{-4} mol/L. Beyond the isoelectric point, the positive mobility increased with increasing concentration of DACL. For the concentrations of n-alkyltrimethylammonium bromide, the isoelectric point tended to shift to the lower concentrations of surfactants with increase in the total number of carbon atoms in alkyl chain. When the Stern-Graham double-layer model was used, the transfer energy of a dissociated molecule with a n-alkyl chain when it moves from a liquid phase to a nitrogen-solution interface was -1.18 $k_B T$.

From Figure 2.1, it can be seen that there were only a few workers who measured the zeta potential of gas bubbles using the sedimentation potential and the streaming potential methods. Usui and Sasaki [19] determined the zeta potential of argon gas bubbles in aqueous solutions of several surfactants, such as sodium hexadecyl

sulphate, and polyoxyethylene dodecyl ether. The sedimentation potential was generated when small gas bubbles were permitted to pass continuously through a column with an inner diameter 2.6 cm and 80 cm long. The bubbles were produced in a range of sizes between 0.2 and 1.0 mm by gas disperser. The sedimentation potential was investigated by examining the difference in electric potential between the point at which the electric potential of bubbles reached a constant value and the point at which the electric potential was zero. The results showed that the absolute values of the zeta potential of bubbles increased with increasing sodium hexadecyl sulphate concentration, from -50 mV at 3 x 10⁻⁷ mol/L to -250 mV at 4 x 10⁻⁵ mol/L. This result agreed with Kubota and co-workers [15] who reported that the absolute values of bubble zeta potential increased with increasing sodium dodecyl sulphate concentration. On the other hand, the zeta potential of bubbles remained nearly constant at -40 mV with increasing polyoxyethylene dodecyl ether concentrations, from 1 x 10^{-5} mol/L to 5 x 10^{-4} mol/L. The bubble diameter in 1-butanol solution is likely to be smaller than in other solutions and the values of zeta potential of bubbles were nearly constant at -20 mV with increasing 1-butanol concentration, in the range from 1 x 10⁻⁴ mol/L to 1 x 10⁻¹ mol/L.

2.2.2 Bubble characteristics

Brandon and co-workers [23] also reported that the rising rate of bubbles in distilled water increased when the bubble diameter was increased. Moreover, the rising rate of bubbles in sodium sulphate at 0.1 mol/L with addition of sulphuric acid, sodium hydroxide and sodium dodecyltrimethylammonium bromide, DTAB, decreased when concentrations of buffer were increased.

Collins and co-workers [14] reported that the terminal velocity of bubbles about 35 μ m in diameter was observed to be 0.05 cm/s. In contrast, Okada and co-workers [16] claimed that the average rising velocities of bubbles were 0.0392 cm/s and 0.191 cm/s for bubbles of 14.4 μ m and 33.1 μ m in diameter, respectively, but the electrophoretic

velocities of those two bubbles of different sizes were almost equivalent. Thus, it might be concluded that the influence of the upward motion of the bubble was small and the zeta potential was independent of bubble diameter in this range. This result was similar to one previously reported. According to Usui and Sasaki [19], McTaggart found that the electric charge at a liquid-gas interface was independent of the nature of the gas bubble and Alty also recognised that the velocity of gas bubbles was independent of the nature of the gas, but depended upon the diameter of the bubble and the purity of the solution. However, Brandon and co-workers [23] mentioned that the electrophoretic mobility depended linearly on bubble diameter in the range 30 to 200 μ m. It would seem that the zeta potential of bubbles is independent of size for very small bubbles but depends linearly on size for larger bubble diameters.

It is clear that the zeta potentials of bubbles in surfactant and chemical solutions may be measured successfully using an electrophoresis technique with bubbles produced by either electrolysis or dissolved-gas methods. The bubble zeta potentials are positive in cationic surfactants and negative in anionic surfactants.

2.3 Particle studies

Coagulation is an important process in which solid particles are agglomerated prior to separation in water and wastewater treatment. Clays in suspension are a common cause of turbidity in surface and ground water. This review will describe coagulation and flocculation of clay particles by using electrolytes and polyelectrolytes such as alum, ferric sulphate and polyaluminium chloride (PAC). The effects of chemical concentrations and pH on electromobility and the removal efficiency of clay particles will also be reported.

2.3.1 Coagulation

Black and co-workers [29-35] conducted electromobility studies on clay and river sediment suspensions using coagulants and polymers. Three types of clays, kaolinite,

montmorillonite and Fuller's earth are generally used as synthetic suspensions for water treatment. Metal ions such as aluminium and ferric were used as coagulants in earlier works [29, 31-33] and the later studies also used polyelectrolytes, polymers and surfactants for coagulation [34-36]. Predictions of optimum coagulation conditions are difficult because of complex reactions between clay suspensions and chemicals to form flocs in suspension. Thus, mechanisms of coagulation by chemical reaction and/or chemical adsorption between coagulants and suspensions continue to be studied.

According to Black and Walters [29], Mattson reported the electromobility of clay particles in 1928 and he suggested that the coagulation of clay suspensions could be investigated using particle charges. However, this concept was rarely used in the water industry or in water coagulation research until Pilipovich and co-workers reintroduced it in 1958. Three types of clay minerals, montmorillonite, kaolinite and Fuller's earth, were studied by measuring electromobility in the absence and presence of ferric sulphate [29] and alum [31]. Black and Walters [29] prepared clay suspensions with sodium bicarbonate (NaHCO₃) added to give a concentration of 50 mg/L. The suspensions were mixed rapidly for 2 min, mixed slowly for 30 min and allowed to settle for exactly 10 min. The turbidity of the supernatant was measured by a colorimeter converted to turbidity units by means of a curve prepared with standard suspensions measured on the Jackson candle turbidimeter. Electromobilities of clay particles were measured by an electrophoretic technique in a Briggs cell. In the absence of coagulants, all three clays exhibited negative charges and nearly constant electromobility of $-2 \ \mu ms^{-1}/Vcm^{-1}$ over the pH range of 3.3-10. This result was similar to that due to Hall [37], who reported that kaolinite suspensions gave negative zeta potentials over the pH range of 4-11. In the case of montmorillonite suspensions with 3 mg/L ferric sulphate added, the negative electromobility was increased slightly and good orthokinetic coagulation occurred in the pH range of 5.5-6.6 giving the minimum residual turbidity. With an increase of ferric sulphate dose to 5 mg/L, the electromobility curve against pH was very similar to the case of 3 mg/L

dose but the zone of good coagulation was broader in the pH range of 4.6-7.8. When the ferric sulphate dose was increased to 50 mg/L, the negative charge was reversed at pH values less than 5.3 and good coagulation obtained with higher pH values. In the case of kaolinite suspensions dosed with 3, 5 and 50 mg/L of ferric sulphate respectively, all particle charges were reversed from negative to positive at pH 6. However, good coagulation was observed for pH values above 4. In the case of Fuller's earth suspensions the electromobility curves and good coagulation conditions were very similar to the results for kaolinite suspensions except that the Fuller's earth suspension with 3 mg/L ferric sulphate gave an isoelectric point at pH 5 and good coagulation in the pH range of 6-7.

When alum is used, the charge on a kaolinite suspension with a dose of 5 mg/L of alum showed a potential reversal from negative to positive at pH 5.3 whereas the other two clays were negatively charged over the pH range of 3.3-10 [31]. The residual turbidity of kaolinite and Fuller's earth were each reduced considerably near pH 8.0, where their electromobilities were negative. When the dosage of alum was increased to 15 mg/L, the charge on kaolinite and Fuller's earth reversed to be positive at the pH range of 4.5-7.5 but montmorillonite was negatively charged over the pH range of 3-10. However, all three clays flocculated well in the pH range of 7.5-8.2 where the particles have a slight negative charge. In the case of 100 mg/L of alum addition, the charges on all three clays reversed to be positive in the range of pH 4.5-7 and suspensions were flocculated well in the pH range of 6-8.5. It is considered that the best turbidity removal of clay suspensions with alum added obtains at pH values of 7.5-8.5 in a region of negative charge rather than at the point of zero charge. This may be explained by noting that precipitated aluminium hydroxides, $Al(OH)_{3(S)}$, present because its isoelectric point is in the pH range of 7.5-8.5 [31, 37], can be adsorbed on clay surfaces.

Black and Chen [33] studied the coagulation of kaolinite suspensions using alum at pH values of 3, 5 and 8. The kaolinite had a cation-exchange capacity of 12.2

meq/100g and a specific surface area of 15.8 m^2/g . The results showed that, at pH 3, the trivalent aluminium ions (Al³⁺) were the most active ion species and the negative charge of clay particles was not reversed below alum concentrations of 50 mg/g. In addition, there was no significant adsorption of the trivalent aluminium ions on clay particles. However, the absolute values of the particle charges decreased from |-2.5|to $|-0.3| \text{ } \mu\text{ms}^{-1}/\text{Vcm}^{-1}$. This may be because the aluminium ions added cause a reduction in the thickness of the double layer. At pH 5, hydrated aluminium multivalent cations such as $Al_6(OH)_{15}^{3+}$, $Al_8(OH)_{20}^{4+}$ were predominant and the negative charges of the clay particles were reversed at a concentration of 5 mg/L of This result might be due to the specific adsorption of excess multivalent alum. aluminium ions on the clay surface. The destabilisation of the clay suspension occurred in a very narrow zone at a point where the electromobility of the clay particles changed from negative to positive. When the alum dose was increased beyond this point, restabilisation was obtained again due to the specific adsorption of the multivalent aluminium ions. At pH 8, aluminium hydroxide was formed and was the major controlling factor in destabilisation. The absolute value of the electromobility of the clay particles decreased from |-3.0| to zero. The destabilisation occurred at alum dosages higher than 40 mg/L and was independent of clay concentration.

Black, Birkner and Morgan [34, 35] studied the destabilisation of dilute kaolinite and montmorillonite clay suspensions using cationic and anionic polymers as coagulating or flocculating agents. For experiments with cationic polymers, kaolinite and montmorillonite suspensions were prepared at approximately pH 7. The jar test and electromobility measurements were described by Black and co-workers [29, 31]. The results showed that the optimum dosage, defined as that which produced maximum destabilisation of the clay suspensions, was increased with increasing clay concentration. The electromobilities of the kaolinite suspensions were increased with increasing cationic polymer dosage and were constant at dosages higher than 0.6 mg/L. However, the electromobilities of kaolinite suspensions at optimum polymer

dosages were negative. The electromobilities of montmorillonite suspensions were similar to the electromobilities of kaolinite ones but the electromobility polymer dosage at the optimum was independent of the clay concentrations.

For experiments with anionic polymers, two kaolinite clay suspensions were prepared with 25 and 250 mg/L CaCl₂, respectively. The electromobilities of the suspensions with anionic polymer present were negative over all the polymer-dosage range. The suspension containing 25 mg/L CaCl₂ gave a more negative charge than the one with 250 mg/L CaCl₂. The destabilisation reaction was influenced by the calcium ion concentration. It was explained that the calcium ions were able to reduce both the repulsive forces between clay particles and the interaction between the adsorbed polymer molecules.

Dempsey and co-workers [36] compared the flocculation behaviour of polyaluminium chloride (PAC) and alum as coagulants in 62.5 mg/L kaolinite clay suspensions. The empirical formula of PAC is $Al(OH)_x(Cl)_y$ where x is a description of the overall degree of hydrolysis of the hydroxy-aluminium products and y = 3-x. The PAC solutions were prepared by dissolving aluminium chloride, $AlCl_3$, in distilled water and adding a predetermined mass of dry sodium bicarbonate, $NaHCO_3$, over a one hour period giving x = 1.80. The jar test conditions were; 3 min rapid mixing, 20 min slow mixing and 60 min quiescent settling. The results showed that PAC was a more effective coagulant than alum in the pH range of 4-10. The PAC dosage used to reduce the particle charges to zero was less than the alum dosage. However, this benefit was less significant at pHs greater than 7.0 due to the increasing hydrolysis of aluminium ions and the greater negative charge on the clay particles.

Solubility diagrams for aluminium and iron compounds are presented in Figure 2.2. When an aluminium salt is added to water, the aluminium hydroxides at equilibrium may form a precipitated aluminium hydroxide, $Al(OH)_{3(S)}$, polymeric species $Al_2(OH)_2^{4+}$, $Al_3(OH)_4^{5+}$, and $Al_{13}O_4(OH)_{24}^{7+}$ and monomeric species such as Al^{3+} ,

AlOH²⁺, Al(OH)₃, and Al(OH)₄⁻ [39, 40]. For iron complexes, the iron hydroxides at equilibrium are Fe(OH)_{3(S)}, a polymeric compound Fe₂(OH)₂⁴⁺ and monomeric species such as Fe³⁺, FeOH²⁺, and Fe(OH)₄⁻. At pH > 10, the soluble species at equilibrium are anions such as Al(OH)₄⁻ and Fe(OH)₄⁻ while, at acidic pH values, pH < 6, the soluble species at equilibrium are cations such as Al³⁺, AlOH²⁺, Fe³⁺ and FeOH²⁺.



Figure 2.2 Solubility diagrams of Al(OH)₃ and Fe(OH)₃ (after Stumm and O'Melia [38]).

Amirtharajah and co-workers [39, 40] also presented coagulation diagrams for aluminium and iron as shown in Figure 2.3 and Figure 2.4. These may be used in the prediction of the appropriate chemical conditions required for the coagulation process. In general, there are four zones in the coagulation diagram namely, stability, adsorption-destabilisation or charge neutralisation, restabilisation, and sweep coagulation. When the amounts of coagulants are very small, coagulation and precipitation cannot occur and this produces a stable colloid suspension. The interaction between the positively charged aluminium hydroxide and negatively charged particles produces two points of zero zeta potential at pHs of 4.8 and 6.8 while the isoelectric point for aluminium hydroxide is at pH of 8.0 as shown in Figure 2.3. Coagulation will obtain at or near the isoelectric point for the colloid suspensions due to charge neutralisation. The restabilisation will occur when the charge on the colloid is reversed by the adsorption of oppositely charged species. The restabilisation zone shows in between two isoelectric points of coated colloid. A zone of sweep coagulation occurs with the precipitated metal hydroxides present giving the optimum condition for coagulation.

Janssens [41] also claimed that restabilisation occurred at very high doses because of the reversal of the charge on the particle. He also reported that adsorptive destabilisation occurred mainly in the cases of high turbidity and low dosages of coagulant, while sweep coagulation obtained in the cases of low turbidity and high concentrations of coagulant.



Figure 2.3 Coagulation diagrams of aluminium (after Amirtharajah and O'Melia [39]).

McCooke and West [42] studied the coagulation of 50 mg/L of kaolinite clay suspension with aluminium sulphate. They simply defined the terms "rapid flocculation", "slow flocculation" and "no flocculation" as a reduction in turbidity of about 85%, 50% and 10%, respectively. After adding aluminium sulphate and acetic

acid, the jar test conditions were; rapidly stirred at 200 rpm for 2 min, slowly mixed at 20 rpm for 1 hour and allowed to settle for 15 min. The rapid flocculation occurred for about 20 mg/L of aluminium sulphate dosage at pH 7.2-7.3 and 160 mg/L of aluminium sulphate dosage at pH 4.6-4.9. The solubility diagram in Figure 2.5 is similar to a diagram presented by Amirtharajah and co-workers [39] in Figure 2.3 but it was produced for a kaolin suspension rather than a colloid suspension. The diagram indicates that the stability of the aluminium ion-pH system is divided into four distinctive zones. Zone (A), the slow flocculation, is on the left hand side while the right hand side is zone (D), no flocculation. Zone (B), central stability, and zone (C), rapid flocculation, are located between zone (A) and (D). The precipitation of aluminium hydroxide occurred in zone (C) giving good coagulation. Zone (B) corresponded to a reversal of charge on the kaolinite particle because of the adsorption of aluminium species. Coagulation in zone (A), which occurred even at zero aluminium dosage, could be explained by the reduction of the negative charge on the kaolinite at low pH. Zone (D) corresponded to the presence of aluminium ion in the form of Al(OH) $_{4}^{-}$ which gave a negative charge again.



Figure 2.4 Coagulation diagrams of iron [39].



Figure 2.5 Coagulation diagram of aluminium (after McCooke and West [42]).

Another factor effecting coagulation is mixing intensity. Janssens [41] reported that Fe^{3+} and Al^{3+} hydrolysis and polymerisation reactions are very rapid (less than one second) but the precipitation of $Al(OH)_3$ occurs in one to seven seconds. Hence mixing between coagulant and suspension should take place within one to seven seconds. If it is carried out for a longer period of time, small flocs will be destroyed. The guideline generally is less than ten seconds. For flocculation, velocity gradient, *G*, and residence time are the important parameters for flocculator design. Residence time is normally varied between 5-30 minutes depending on floc characteristics. However, mixing conditions will be summarised in section 2.4 where practical details are described.

Clearly, the zeta potentials of montmorillonite and kaolinite suspensions in the absence of coagulants are negative over the pH range of 3-10. Good coagulation using coagulants is usually obtained when the zeta potentials of the particles are slightly negative. The hydrolysed metal solubility diagram is an important tool used

to explain the mechanisms of coagulation and flocculation in the complex reactions of metal hydrolysis.

2.3.2 Floc strength and breakage

Floc strength can be defined indirectly as the maximum or mean floc diameter of an equilibrium floc size under an agitation condition [43]. The floc size distributions can be observed directly using a microscope or analysed using floc photographs [44]. Although this technique gives a good result, it takes time and it is difficult to identify some aggregates that form translucent networks such as bentonite flocs formed with ferric chloride. Alternative techniques for the characterisation of aggregates have been introduced in recent years. These include particle size measurements from an electrical sensing method (Coulter counting) [45], a light obscuration technique, the HIAC Royco [46], and scanning laser microscopy (Lasentec) [47]. It seems that a scanning laser microscopy technique is a convenient method because a sensor can be fitted in-line with the reactor or mixing tank.

Peng and Williams [47] investigated floc breakage in a stirred tank and a flow tube reactor but only the test in the mixing tank will be described. The stirred tank of 5 L volume and 180 mm diameter was fitted with four baffles, each 180 mm wide. A sixbladed disc turbine impeller of 60 mm was mounted in the tank. The sensor of the scanning laser microscope apparatus was placed in a vertical position 10 mm from the side wall of the tank and 30 mm above the impeller. After adding coagulant, particle size distributions were measured every 8 seconds continuously. The energy input to the tank was estimated using power number calculations [6]. Their results showed that Flocs of both polystyrene latex and silica were easily broken up when the agitator speed was increased but fragments of the broken flocs could reaggregate slowly when the shear rate was reduced. It seems that floc breakage is a reversible process and a mean equilibrium floc size is determined by the specific conditions obtaining. The mean equilibrium floc size not only depends on process variables such as coagulant

dose and pH but it is proportional to shear gradient (see more details in section 3.7.2). This result will be confirmed again by the experiments reported in section 7.5. The mechanisms of floc breakage are not fully understood but rupture of flocs is thought to occur with loose aggregates and an erosion mechanism is more likely to be the case with dense aggregates.

2.4 Flotation processes

In general, dissolved air flotation, DAF, is a batch process on a small scale but on a large scale it is a continuous one. DAF normally comprises coagulation at high mixing speeds, flocculation at low mixing speeds and separation in a flotation tank. Although many parameters such as a nozzle and a saturator efficiency are important in the analysis of DAF performance, the main objective here is to discuss operating conditions in both batch and pilot-scale flotation.

Coagulation and flocculation are important primary processes in DAF treatment. Zabel [3] indicated that an optimum pH and coagulant dosage were required for water treatment, which was supported by Hyde and co-workers [48]. In general, the optimum velocity gradient, *G*, for coagulation was reported to be in the range of 70-400 s⁻¹ for surface water treatment and the shear rate for good flocculation was about 10-70 s⁻¹. A baffled tank flocculator needs a shorter detention time than an unbaffled tank and the tip speed of the paddles should not be more than 0.5 m/s to avoid floc breakage. This range of velocity gradients is in agreement with those quoted in Edzwald's report [49] where design and operating parameters are summarised, see Table 2.1. The optimum value of the velocity gradient depended on the type of chemical, for example 70-80 s⁻¹ for alum, 70 s⁻¹ for ferric chloride and greater than 30 s⁻¹ for PAC. On low turbidity testing of various water sources Edzwald and coworkers also found that the optimum shear rate was in the range of 55-100 s⁻¹ using alum and PAC as coagulants.

Parameters	South	Finland	Nether-	UK	UK	Scandi-
	Africa		lands			navia
Flocculation						
- time [min]	4-15	20-127	8-16	20-29	18-20	28-44
Flotation reaction zone						
- time [min]	1-4	-	0.9-2.1	-	-	-
- overflow [m/hr]	40-100	-	50-100	-	-	-
Flotation separation zone						
- overflow [m/hr]	5-11	2.5-8	9-26	-	-	-
Total flotation area						
- time [min]	-	-	-	-	11-18	-
- overflow [m/hr]	-	-	10-20	5-12	8.4-10	6.7-7
Recycle ratio [%]	6-10	5.6-42	6.5-15	6-10	. 5-10	10
Unpacked saturator						
- pressure [kPa]	400-600	-	-	-	400-550	460-550
Packed saturator						-
- pressure [kPa]	300-600	-	-	-	400-500	-

Table 2.1	Summarv	of DAF	design ar	nd operating	parameters	[49].
14010 2.1	Sammary	or D/H	uesign ui	ia operaning	Pulumeters	['/]

The flocculation time for drinking water treatment in South Africa was recommended at 4-15 min, which agreed with data from the Netherlands. In the UK and the Scandinavia, on the other hand, the flocculation time for similar operation was about 20 min or more.

A circular column is generally used in small scale flotation work, while a rectangular flotation tank is normally used in large scale operations with a depth of about 1.5 m depending on the tank surface area. In general, a high overflow rate or a short detention time is specified for the reaction zone and long detention time for the separating zone. The typical range of detention times in the flotation tank was 5 to 15 min and the overflow rate was given in the range of 40-100 m/hr for the reaction zone

and 5-12 m/hr for the separating zone [3, 49, 50]. This is indicates that the kinetics of bubble collision and attachment are fast.

Both packed and unpacked saturators are used for DAF but packed saturators are more generally applied, giving an efficiency of up to 90 % [51]. With the packed saturator, an operating pressure in the range of 350-420 kPa and a recycle ratio of 7-8% can produce air to about 8-10 mg/L [3]. However, Malley and Edzwald [50] reported that a saturator pressure at 70 psig with an 8% recycle ratio was able to produce air concentrations of 7.5 and 5.5 mg/L at 4 and 20°C, respectively. These different results may be caused by the differences in saturator efficiency and other conditions such as water quality and temperature. The overflow rate of packed saturators could be operated in the range of 12.5-83.3 m/hr without decrease in saturation efficiency [3]. The bubble volume concentration can be controlled by varying the saturator pressure or recycle ratio or both.

Nozzles and needle valve are simple devices used to release saturated water from a pressure vessel. Since fine bubbles coalesce behind such equipment, air must be released very close to a point where the saturated water is mixed with the suspension.

The quantity of air required for the treatment of raw water can be represented by a recycle ratio or an air to solid ratio. For example, recycle ratios were reported as varying between 6 % and 10 % [48-50] depending on the suspension characteristics and operating conditions. The air to solid ratio used was about 380 ml of air to one gram of solids for water treatment and 15-30 ml of air per gram of solids for activated sludge thickening [3].

DAF has been used to remove suspended solids from both synthetic and natural waters in laboratory and pilot scales, with results which can be summarised as follows.

Hyde and co-workers [48] studied the removal of contaminants in laboratory and pilot scale tests using flotation processes developed by the Water Research Centre, WRC. In laboratory studies, three 1.2 litre-vessels were used for coagulation and flocculation processes. Each vessel was connected to a manifold fixed to its base where water saturated with air at pressures up to 690 kPa was injected. The release devices or solenoid valves were controlled by timers. The test conditions were rapid mixing for 1 min and slow mixing for 15 min at 20 rpm. The saturated water was allowed to flow into each vessel and the paddle flocculator was stopped for 10 min before a sample was removed for analysis. The results showed that large and low density flocs, generally, were floated more effectively than small flocs resulting from the use of an inadequate coagulant dosage. It is important to avoid floc breakage when air is released in the suspension. The quantity of dissolved air required to float this floc was represented by a recycle ratio of 6 % by volume of water saturated with air at 345 kPa.

In pilot plants, two scales of operation were investigated using River Thames water. The plants consisted of a flash mixer, a four-stage mechanical flocculator, a flotation tank and a sand filter. The first pilot plant had a capacity of 1.8 m³/hr and used clean water in its pressurising unit. It was reported that DAF was a technically feasible alternative to sedimentation for water clarification of low land water, such that found in the River Thames. Effective treatment of Thames water was achieved at 4-6 % recycle ratio by using clean water saturated with air at 345 kPa. The second pilot scale unit used treated-water from the flotation tank as recycle. Therefore, the recycle ratio had to be increased slightly to 7% by volume for a successful treatment. The water was dosed with alum or FeCl₃, mixed for 1.5 min in a flash mixer, slowly mixed for 9 min in the flocculator and passed through the flotation tank for a residence time of 5.5 minutes. The rapid sand filter was operated at a flow rate of 2 mm/s. The solid content of the sludge removed from the flotation tank was independent of the tank and raw water turbidity.

Malley and Edzwald [50] studied the flotation of synthetic water and natural waters from Washington Mountain Brook and Upper Root Reservoir. Some details are given in Table 2.2.

	Synthetic suspension			Natural raw water			
Parameter	Clay 20 mg/L in FA* [mg/L]			Wash	ington	Upper Root	
	0	. 2	10	M. E	Brook	Reservoir	
Temperature [°C]	-	-	-	24	4	24	4
рН	7.0	7.0	7.0	6.68	6.28	7.51	7.59
Turbidity [NTU]	1.31	1.29	1.34	1.46	0.60	1.66	1.05
True colour [pt-co]**	-	23	105	158	45	17	18
Total alkalinity [mg/L]	-	-	_	20.0	3.0	65.0	70.0
Total hardness [mg/L]	-	-	-	20.0	3.0	72.0	74.0
Calcium [mg/L]	-	-	-	-	2.0	52.0	56.8

Table 2.2 Suspension data for synthetic and natural raw waters [50].

* FA is the fulvic acid

** True colour is defined as water colour due to dissolved substances which it is compared to the mixtures of potassium chloroplatinate, K_2PtCl_6 , and cobaltous chloride, $CoCl_2 \bullet 6H_2O$.

The synthetic water was made with montmorillonite clay at a concentration of 20 mg/L mixed with fulvic acid (FA) at pH 5.0 for 24 hours. The operating conditions for flotation and conventional gravity separation (CGS) experiments are given in Table 2.3. The results showed that the residual turbidity from the DAF process was significantly lower than that from the CGS for both synthetic and natural suspensions, especially at low temperature. The recycle ratio of DAF was 8% (483 kPa of saturation pressure) which is a normal value when dealing with low turbidity suspensions. The overflow rate of the DAF process was six times higher than that of the CGS. Moreover, the tests of the effect of flocculation time on turbidity removal for Washington Mountain Brook's water using alum as coagulant showed that the

flocculation time did not significantly affect the DAF performance while in contrast the CGS required a flocculation time of at least 20 min.

Table 2.3 Operating conditions used for experiments comparing DAF and conventional gravity separation CGS [50].

Parameter		DAF	CGS
Rapid mix	Time [min]	2	2
	Speed [rpm]	400	400
	G [s ⁻¹]	380	380
	Gt [-]	45,600	45,600
Flocculation	Time [min]	20	20
	Speed [rpm]	30	30
	<i>G</i> [s ⁻¹]	10	10
	Gt [-]	12,000	12,000
DAF and CGS	Time [min]	10	60
	Sample volume [L]	1	1
	Overflow rate [m/hr]	0.84	0.14
	Saturation pressure [kPa]	483	-
	Saturation efficiency [%]		-
	Recycle ratio [%]	8	-
	Temperature [°C]	22-25	22-25

Edzwald and co-workers [51] studied flocculation and air requirements for synthetic water and natural water from Lake Whitney, USA, in bench and pilot scale flotation tests. In the bench scale tests, the flocculation conditions were: rapid mixing for 2 min at 400 rpm (G of 380 s⁻¹) and slow mixing at 30 rpm (G of 10 s⁻¹) for 5, 10 or 20 min. Ultrapure water saturated with air at 483 kPa was fed into the flotation tank for 10 min before a sample was taken. The results of these trials showed that big flocs were not necessary for good DAF treatment but very good clarification was achieved with small flocs. The air required for DAF to give a residual turbidity of 1 NTU or less is given in

Table 2.4. Tests with natural water showed that alum at 28 mg/L and ferric chloride at 20 mg/L were sufficient to achieve destabilisation. The results of the tests with alum showed that a 5% recycle ratio was sufficient to remove turbidity to less than 1 NTU and achieve 65% removal of algae. The results of tests with ferric chloride added gave 70% and 90% removal efficiency of algae for recycle ratios of 5% and 8%, respectively and the residual turbidity was still less than 1 NTU. In a pilot plant, a two-stage flocculator was used for three experiments, namely one without flocculation, one using simple stage flocculation at a mean residence time of 8 min and a third with two-stage flocculation at a mean residence time of 16 min. The natural water was tested at 10% recycle ratio using treated water from the flotation tank for recycle. The average turbidity of the raw water was 5.2 NTU and ferric chloride was used as the coagulant in a concentration range of 23-27 mg/L. The results with no flocculation showed that DAF treatment performance was poor but one-stage and two-stage flocculation were able to reduce turbidity to 0.4-0.5 NTU.

Water type	Concentration	Flocculated	To achieve 1 NTU or less			
	-	Turbidity [NTU]	Recycle [%]	Bubble vol. conc. [ppm]		
clay	20 mg/L	8.8	6.5	3760		
clay	100 mg/L	58.3	8	4560		
fulvic acid	2 mg DOC*/L	2.3	4.5	2650		
fulvic acid	5 mg DOC/L	8.9	8	4560		
fulvic acid	15 mg DOC/L	26.2	8	4560		
algae	$2 \ge 10^4$ cells/ml	0.6	5	2930		
algae	1 x 10 ⁵ cells/ml	1.5	5	2930		
algae	5 x 10 ⁵ cells/ml	9.8	5	2930		

Table 2.4 Air requirements for several types of water [51].

*DOC : Dissolved organic carbon

Johnson and co-workers [52] reported the results of pilot scale flotation treatment compared with other alternative treatments for the Massachusetts Water Resources Authority, in the USA. Two-stage coagulation was operated at the maximum flow of 171 m/hr and each flocculator had a detention time of about 10 min. The velocity gradients were 70 s⁻¹ for the first stage and 40 s⁻¹ for the second stage. The saturator was maintained at 484 kPa and recycle ratios varied between 4 to 8%. The results showed that DAF was able to reduce the turbidity to 0.1 NTU in over 90% of the runs. Another significant benefit of DAF is the reduction in ozone demand when ozone is added to meet a disinfection requirement. In pilot testing it was found that by using DAF before ozonation, the design capacity of the ozone facility could be reduced from 3.5 to 2.0 mg/L.

Research and development on most aspects of DAF for water treatment has been conducted in many countries such as the UK [53], the USA [54], the Netherlands [55], South Africa [56] and others [57]. It seems that DAF is becoming an increasingly popular approach to solid liquid separation for drinking water treatment.

Chapter 3

Theory

3.1 Introduction

The flotation process is considered as a complicated mechanism due to the interaction between the three phases in the process. The interaction of surface forces and the hydrodynamic interaction around the rising bubbles are controlling parameters. Thus, it is important to consider the relevant concepts of surface chemistry which will be explained in this chapter including the double layer theory, the electrokinetic theory, polar and nonpolar forces, adsorption at interfaces, and coagulation and flocculation processes.

3.2 Flotation processes

Flotation processes can be divided into five types [58], namely dissolved air flotation (DAF), vacuum flotation, bubble air flotation, froth flotation and electrolysis flotation. Each type of flotation is different in its method of producing air bubbles. In DAF, clarified or clean water is pressurised to 4-6 atmospheres in a pressure vessel. When this pressurised air-liquid solution is released to atmospheric pressure in a collecting tank or flotation cell, fine bubbles, 10-100 μ m, are released into the solution. On the other hand, vacuum flotation is the process in which the suspension will be saturated with air at atmospheric pressure before flowing through the vacuum flotation-cell. Then, the fine bubbles are released from the solution by a pressure difference. Electrolysis flotation or electroflotation is a process which uses direct current electricity to generate fine bubbles which are similar in size to the fine bubbles from DAF. Bubble air flotation is a process which supplies air by air-compressor through the porous media or sparger to produce air bubbles. Finally, froth flotation generally uses a mechanical agitator to produce air bubbles. The latter

two processes, bubble-air and froth flotation, normally produce a large air bubble size of approximately 1-2 mm. In general, DAF is most widely used in clarification processes and potable and wastewater treatment because of high efficiency, easy operation and reasonable cost investment.

Four modes of operation [59] are possible, as shown in Figure 3.1 i.e. full-stream pressurisation, split-stream pressurisation, recycle-stream pressurisation with clean effluent and pressurisation with clean water. Modes (c) and (d) are typically used because of the higher efficiency of air-solubility in water and less breakage of floc under pumping processes. In modes (a) and (b), the amount of air released is lower than amount of air in modes (c) and (d) because the solubility of air in water is reduced due to contaminants in the suspension.

The amount of air released from water saturated at a pressure P when reduced to atmospheric pressure can be calculated from Henry's law given by

$$A_d = K(P-1) \tag{3.1}$$

where A_d is the amount of air released, K is Henry's constant and P is the absolute pressure. When this equation is applied to the flotation cell in recycle mode, the result is

$$A'_d = R_0 f K(P-1) \tag{3.2}$$

where A'_d is the amount of air released in the flotation cell, R_o is the recycle flow rate and *f* is the efficiency of the saturation-desaturation process.

In unit time, the amount of solids in contact with the air rate given in equation (3.2) is

$$S_{wt} = Q_v c_s \tag{3.3}$$

where S_{wt} is the weight of solid inflow, Q_v is the volumetric flowrate of suspension and c_s (wt/vol) is the solid concentrations in suspension.



Figure 3.1 DAF systems (a) full-stream pressurisation, (b) split-stream pressurisation,(c) recycle-stream pressurisation with effluent and (d) pressurisation withclean water.

Thus, the air to solid ratio A_s is

$$A_s = \frac{R_o f K(P-1)}{Q_v c_s}$$
(3.4a)

or

$$R_{\rm o} = \frac{A_s Q_v c_s}{f K(P-1)}$$
(3.4b)

The recycle ratio or air to solid ratio is a parameter that represents the amount of air or bubble number in the system. Since the major energy cost of DAF arises from the pressurisation unit, an optimum recycle ratio is usually sought in each operation.

3.3 Flotation kinetics

The overall rate of removal of solids by flotation might be represented in a first order kinetic equation given as [60]:

$$\frac{\mathrm{d}N_p}{\mathrm{d}t} = -k_1 N_p \tag{3.5}$$

where k_1 is the rate constant and N_p is the particle number concentration. The rate constant was given as a function of collision efficiency, η_c , attachment efficiency, η_a , and bubble number concentration in the form :

$$\frac{\mathrm{d}N_p}{\mathrm{d}t} = -(\eta_c \eta_a)(A_b u_b N_b)N_p \qquad (3.6)$$

where A_b is the projected area of a bubble, u_b is the bubble velocity, and N_b is the bubble number concentration.

For a batch flotation process, the bubble velocity is given as $\frac{dH_t}{dt}$ where H_t is the particle height in the column. Hence :

$$\frac{\mathrm{d}N_p}{\mathrm{d}H_t} = -(\eta_c \eta_a)(A_b N_b)N_p \qquad (3.7)$$

If this equation is integrated over the column height, the overall rate of removal of solids by flotation is given as

$$1 - \frac{N_p}{N_{p0}} = 1 - \exp\{(-\eta_c \eta_a)(A_b N_b)H_t\}$$
(3.8)

For a continuous flotation process, if the average bubble velocity is given as the relative bubble velocity compared with the suspension velocity in the column, equation (3.6) can also use to calculate the removal efficiency of particles. The overall rate of removal of solids by the continuous flotation process is given as

$$1 - \frac{N_p}{N_{p0}} = 1 - \exp\{(-\eta_c \eta_a)(A_b u_b N_b)\tau\}$$
(3.9)

where τ is the retention time of the suspension in the column. Thus, a flotation efficiency can be calculated using equation (3.8) for a batch test and equation (3.9) for a continuous process.

3.4 Double layer theory

According to Collins and Jameson [13], the effect of particle charge in the flotation process was studied by Jaycock and Ottewill who found that the flotation efficiency was at its highest value when the zeta potential of silver iodide particles was zero. The zeta potential is an important parameter, which is responsible for the stability and instability of colloidal suspensions [61]. There are many applications in which the zeta potential is used as indicative parameter. For example, zeta potential is used when studying the mechanism of adsorption of solutes at particle interfaces,

investigating the stability of emulsion paint and in finding the isoelectric point. In addition, the zeta potential is often used when considering the destabilisation of suspended particles in coagulation and flotation processes. It is considered that the coagulation process normally reaches its highest aggregation value at the isoelectric point where the zeta potential is zero. De Vivo and Karger [62] found such a result with clay particles. Moreover, Okada and co-workers [17] showed that the flotation efficiency had the highest value when the zeta potential of both the bubbles and particles attained their lowest absolute values or their isoelectric point. To explain the zeta potential concept, the electric double layer theory will be described in this section. The zeta potential or the surface charge can be measured using several different techniques; each method is based on an electrokinetic effect as explained in a following section.

The electric double layer at the surface of particles can be considered as consisting of two regions according to the Stern model i.e. an inner region which may include adsorbed ions and an outer or diffuse region. The diffuse layer is the region in which ions are distributed due to the influence of electrical forces and random thermal motion as described by the Gouy-Chapman theory. However, the inner region of Stern layer can be sub-divided into the inner Helmholtz plane (IHP) and the outer Helmholtz plane (OHP) according to the Stern-Grahame model [63].

3.4.1 Gouy-Chapman model

Gouy-Chapman model or the electric double layer model was represented in a diffuse region based on the follow assumptions:

- 1. The surface of particle is flat, infinite and the charge uniform.
- 2. The ions in the diffuse region are point charges following the Boltzmann distribution.
- 3. The medium has uniform properties.
- 4. A single symmetrical electrolyte will be considered.
(3.9b)

When the electric potential at a flat surface is φ_0 and at a distance x from the surface in the electrolyte solution is φ , the Boltzmann distribution is given by equation (3.9)

$$n_{+} = n_0 \exp\left[\frac{-ze\varphi}{k_{\rm B}T}\right]$$
 (3.9a)

and

where n_+ and n_- are the respective number of positive and negative ions per unit volume at points where the potential is φ , n_0 is the bulk concentration of each ion, z is the ion valency of electrolyte, e is the electron charge, T is temperature and k_B is Boltzmann constant.

The net volume charge density ρ at points where the potential is φ described by

$$\rho = ze(n_+ - n_-)$$

 $n_{-} = n_0 \exp\left[\frac{+ze\phi}{k_{\rm B}T}\right]$

$$= zen_0 \left\{ \exp\left[\frac{-ze\varphi}{k_BT}\right] - \exp\left[\frac{+ze\varphi}{k_BT}\right] \right\}$$
$$= -2zen_0 \sinh\left[\frac{ze\varphi}{k_BT}\right]$$
(3.10)

From Poisson's equation [63], the final result gives the charge distribution as

$$\varphi = \frac{2k_BT}{ze} \ln\left[\frac{1+\gamma_c \exp(-\kappa x)}{1-\gamma_c \exp(-\kappa x)}\right]$$
(3.11)

where

$$\gamma_c = \frac{\exp[ze\varphi_0 / 2k_B T] - 1}{\exp[ze\varphi_0 / 2k_B T] + 1}$$
(3.12)

(3.16)

and
$$\kappa = \left[\frac{2e^2n_0z^2}{\epsilon k_BT}\right]^{1/2} = \left[\frac{2e^2N_ACz^2}{\epsilon k_BT}\right]^{1/2}$$
 (3.13)

κ is the Debye-Huckel parameter, N_A is the Avogadro number = 6.0225 x 10²³ mol⁻¹ and C is the ion concentration.

If
$$\left[\frac{ze\varphi_0}{2k_BT}\right] \ll 1$$
, the Debye-Huckel approximation is

$$\exp\left[\frac{ze\varphi_0}{2k_BT}\right] \cong 1 + \left[\frac{ze\varphi_0}{2k_BT}\right]$$

then $\varphi = \varphi_0 \exp(-\kappa x)$

Another important result from the Gouy-Chapman theory is the relation of surface charge density σ_0 to the surface potential ϕ_0 , where the surface charge must be balanced by the excess charge in the diffuse layer. From charge density defined as $\sigma_s = -\int_0^\infty \rho dx$ and the Poisson-Boltzmann distribution, the result for the diffuse layer is

$$\sigma_s = (8n_0 \varepsilon k_B T)^{1/2} \sinh\left[\frac{ze\varphi}{2k_B T}\right]$$
(3.17)

It is considered that the surface potential depends on the surface charge density and the ionic composition of the solution included in the Debye-Huckel parameter κ .

3.4.2 Stern model

Stern (1924) proposed a model in which the double layer is divided into two parts separated by a plane located at about a hydrated ion radius from the surface. This

plane defined the limit of the Stern layer. The electrical potential difference between the particle surface and the bulk solution is called the Nernst potential, φ_0 , which drops linearly across the Stern layer from φ_0 to φ_d , which is named the Stern potential. From this point, the electrical potential will decrease exponentially with increasing distance from the particle to the bulk solution where the potential is zero. When specific adsorption is obtained, a double layer of counter-ions is postulated as shown Figure 3.2. For surfactant adsorption, φ_d may have the opposite or same sign as φ_0 depending on the type of adsorbed surfactant as shown in Figure 3.3. The zeta potential is the electrical potential which is measured at the plane of shear between the particle surface and the bulk solution. However, the exact position of this shearing plane is not known, but it is normally assumed to be in the diffuse layer.



Figure 3.2 The electric double layer following Stern model (after Shaw [63]).





(b) A Stern potential with a higher value than the Nernst potential due to the adsorption of surfactant co-ions.

3.4.3 Stern-Grahame model

Grahame (1947), subdivided the Stern layer into two regions i.e. an inner layer occupied by specifically adsorbed ions and an outer layer where counter-ions are located. The boundaries of these regions are often known as the inner Helmholtz plane (IHP) and the outer Helmholtz plane (OHP). The OHP is equivalent to the Stern plane and outside this plane is the diffuse layer described by the Gouy-Chapman model. This approach shows that the inner layer is occupied by specifically adsorbed unhydrated ions and in the outer layer are located by hydrated ions [64]. When ions are adsorbed on the inner Helmholtz plane a corresponding surface charge will be created. This modelling is often used for oxide-water interfaces giving a triple layer model [65].

3.5 Electrokinetic theory

This section will discuss the methods of making zeta potential measurements, namely, by electrophoresis, sedimentation potential or streaming potential.

3.5.1 Electrophoresis

The theory of electrophoresis can be used to calculate the zeta potential from measurements made by all electrophoresis sub-techniques. These equations are derived simply from the electro-osmosis process which is the phenomenon of the liquid movement under the influence of the applied electric field. Smoluchowski derived an equation for electro-osmosis behaviour which described the movement of the liquid between two parallel flat plates, charged by an electric field along the fixed surfaces [18, 66]. If the surface is negatively charged, there will be a net excess of positive ions in the adjacent liquid moving under the influence of the applied field, which will draw the liquid along with them. According to double layer theory, the plane of shear in this case may be taken as a plane parallel to the surface and distant δ from the wall as shown in Figure 3.4a. The velocity of the liquid at steady state in the direction parallel to the wall, v_z , increases from zero in the plane of shear to a maximum velocity, v_{eo} , at some distance from the wall. This velocity is called the electro-osmotic velocity of the liquid. On the other hand, the electrostatic potential decreases from the zeta potential in the plane of shear to zero at some distance from the wall. In addition, Figure 3.4b shows the forces on an element of volume of the liquid with thickness dx and area A under the influence of an electric field. The rate of

momentum transfer out the across surface x is $\mu A \left(\frac{dv_z}{dx}\right)_x$ and the rate of momentum in across the surface x+dx is $\mu A \left(\frac{dv_z}{dx}\right)_{x+dx}$. The net rate of momentum transfer in the z-direction is E_zQ where E_z is the field strength and Q is the charge. Then, the differential equation can be summarised in equation (3.18).

In the z-direction

$$E_Z Q = E_Z \rho A dx = \mu A \left(\frac{dv_z}{dx}\right)_x - \mu A \left(\frac{dv_z}{dx}\right)_{x+dx}$$
(3.18)

where μ is the viscosity of the medium and ρ is the charge density related to the ion concentration as follows [18]:

$$\rho = \sum_{i} n_{i} z_{i} e = -4\pi\varepsilon_{o} \frac{D}{4\pi} \left(\frac{d^{2} \varphi}{dx^{2}} \right) \qquad (3.19)$$

where *n* the number of particles, *z* is the ion valency of electrolyte, *e* is the elementary electric charge = 1.6021×10^{-19} [C], *D* is the dielectric constant and ε_0 is the permittivity at free space = 8.854×10^{-12} [F/m].



Figure 3.4 *a*) The liquid velocity and electrostatic potential profile at any distance from the surface of the plate under an applied electric field.

b) Forces on an element of the liquid of area A containing charge Q [18].

When equation (3.18) is rewritten, the differential equation is given as follows :

$$E_{Z} 4\pi\varepsilon_{o} \frac{D}{4\pi} \left(\frac{d^{2} \varphi}{dx^{2}} \right) dx = \mu \left(\frac{d^{2} v_{z}}{dx^{2}} \right) dx \qquad (3.19)$$

The boundary conditions are

B.C. 1
$$\frac{d\phi}{dx} = \frac{dv_z}{dx} = 0$$
 at $x = \infty$
B.C. 2 $\phi = 0$ at $v_z = v_{e0}$ and $\phi = \zeta$ at $v_z = 0$

Then, the solution is

$$\frac{v_{e0}}{E_Z} = U_{em} = -4\pi\varepsilon_o \frac{D\zeta}{4\pi\mu} = -\frac{\zeta\varepsilon}{\mu}$$
(3.20)

where ζ is the zeta-potential and U_{em} is the electromobility.

However, this analysis of electro-osmosis behaviour can be applied also to the electrophoretic motion but in that case the particle moves in the stationary fluid. Then, the result is

$$U_{em} = 4\pi\varepsilon_o \frac{D\zeta}{4\pi\mu} = \frac{\zeta\varepsilon}{\mu}$$
 for $\kappa r_p > 200$ (3.21)

where r_p is the particle radius.

This is called Smoluchowski's equation for electrophoretic mobility which is used for large particles and strong electrolytes ($\kappa r_p > 200$). κr_p is dimensionless and κ represents the reciprocal thickness of the double layer (κ^{-1} is the double layer thickness or Debye length). The value of κ^{-1} depends on the electrolyte type and concentration, and increases with decreasing electrolyte concentration.

At low ionic strength and particle sizes, Huckel proposed an equation in the form

$$U_{em} = 4\pi\varepsilon_{\circ}\frac{D\zeta}{6\pi\mu} = \frac{2\zeta\varepsilon}{3\mu}$$
 for $\kappa r_p < 0.1$ (3.22)

The electrophoretic mobility in the intermediate range of κr_p (0.1 to 200) can be expressed as

$$U_{em} = \frac{2\zeta\epsilon}{3\mu} [1 + f(\kappa r_p)]$$
 for 0.1 < κr_p < 200 (3.23)

where $f(\kappa r_p)$ is the correction factor taking values as follows:

кr _p	0	0.1	1	5	10	50	100	>200
$f(\kappa r_p)$	0	0.001	0.027	0.160	0.239	0.424	0.458	0.500

Equation (3.23) is known as Henry's equation [67].

3.5.2 Sedimentation potential technique

According to Hunter, [18] when a particle is moving through a liquid, a continuous flow of ions will occur from the bulk solution to the particle double layer. These ions also flow around the particle surface and return to the bulk from the surface. In the steady state, the two currents are equal and shown in equation (3.24)

$$nv_Z Q = E_Z \lambda \tag{3.24}$$

where *n* is the number of particles per unit volume and λ is the specific conductance of bulk solution.

From Stokes' Law and the electrokinetic charge on particle [18], the zeta potential can be given in equation (3.25) as :

$$\zeta = \frac{3\lambda\mu E_z}{4\pi\epsilon_0 Dnr_p^3(\rho_p - \rho_m)gL} \quad \text{when } \kappa r_p >> 1 \quad (3.25)$$

where r_p is the radius of the particle, ρ_p is the density of the particle, ρ_m is the density of the medium, L is the distance between electrodes with which the sedimentation potential was measured, and g is the gravitational constant.

According to Usui and co-workers [19], the relation between the zeta potential and the sedimentation potential is given by Davis and co-workers in equation (3.26)

$$\zeta = \frac{4\pi H_L \lambda \mu \Delta E}{(\rho_p - \rho_m)g \varepsilon \Delta H L}$$
(3.26)

where ΔE is the sedimentation potential, H_L is the height of the liquid column in which the dispersed phase is introduced and, ΔH is the increment of the liquid column height upon the introduction of the dispersed phase.

Equation (3.26) can be used to calculate the zeta potential of particles using the sedimentation potential technique.

3.5.3 Streaming potential technique

The streaming potential is generated by fluid flow over solid surfaces such as capillaries and porous media. From the velocity profile of the liquid flowing in the capillary, Poiseuille's equation (3.27) is given and the relation between the streaming current, I_{st} , and the zeta potential may be obtained from equation (3.28) [18].

$$v_z = \frac{\Delta P(R_i^2 - r^2)}{4\mu L}$$
 (3.27)

$$I_{st} = -\frac{\varepsilon_0 \varepsilon \pi R_t^2 \Delta P}{\mu L} \zeta \qquad (3.28)$$

where ΔP is the pressure gradient, R_i is the capillary diameter and I_{si} is the streaming current at a stationary level.

3.6 Adsorption at interfaces

Surface active agents such as short-chain fatty acids and alcohols are soluble in both water and oil. The non-polar hydrocarbon parts of the molecules are normally soluble in oil, while the polar -COOH or -OH groups are incorporated into the water phase. In the case of the air-surfactant solution system, the hydrophilic head groups of the surfactant molecules are located in the liquid phase, while the non-polar hydrocarbon chains are transferred into the vapour phase [63].

Molecules of surface active materials or surfactants have both polar and non-polar parts. It is considered that the activity on the interface between a solution and a particulate material is a dynamic phenomenon. For surfactant solutions at equilibrium, the energies of the surfactant molecules adsorbed onto an interface must be balanced against the surface tension forces. The surface tension measured in the presence of an adsorbed surfactant is normally lower than that obtained in the absence of adsorption. In the case of electrolyte and sugar solutions, however, the surface tension of these solutions is slightly increased as their concentrations are increased due to negative ion adsorption. This may explain why the solute molecules tend to move away from the surface into the bulk solution because the solute-solvent attractive forces are greater than the solvent-solvent attractive forces.

3.6.1 Gibbs adsorption equation

The adsorption between two phases can be described in the terms of surface excess concentrations defined as [63]

$$\Gamma_i = \frac{n_i^{\sigma}}{A_i} \tag{3.29}$$

where Γ_i is the surface excess concentration of component *i*, n_i^{σ} is the amount of component *i* in the surface phase σ and A_i is the interfacial area.

From thermodynamic theory, the total energy of a system is given by the expression

$$U = TS_T - PV_T + \Sigma \mu_i n_i \qquad (3.30)$$

where P is the total pressure of system, V_T is the total volume, S_T is the total entropy and μ_i is the chemical potential of component *i*, and thermodynamic energy of a surface phase σ is

$$U^{\sigma} = TS^{\sigma} - PV^{\sigma} + \gamma A_i + \Sigma \mu_i n_i^{\sigma}$$
(3.31)

At constant temperature and pressure, the final result is

$$d\gamma_L = -\Sigma \frac{n_i^{\sigma}}{A_i} d\mu_i = -\Sigma \Gamma_i d\mu_i \qquad (3.32)$$

For simple two-component solution denoted by A as solvent and B as solute, equation (3.32) can be written as

$$d\gamma_L = -\Gamma_A d\mu_A - \Gamma_B d\mu_B \qquad (3.33)$$

The surface excess concentration of the solvent, Γ_A , is zero, then

$$d\gamma_L = -\Gamma_B d\mu_B \tag{3.34}$$

and

$$d\mu = R_g T d[\ln a_c]$$

where a_c is the chemical activity and R_g is gas constant. Substitution of chemical potential with activities gives the following equation

$$\Gamma_B = -\frac{1}{R_g T} \frac{\mathrm{d}\gamma_L}{\mathrm{d}[\ln a_{cB}]} = -\frac{a_{cB}}{R_g T} \frac{\mathrm{d}\gamma_L}{\mathrm{d}a_{cB}}$$
(3.35)

where a_{cB} is the chemical activity of solute.

For a dilute solution

$$\Gamma_B = -\frac{1}{R_g T} \frac{\mathrm{d}\gamma_L}{\mathrm{d}\ln C_B} = -\frac{C_B}{R_g T} \frac{\mathrm{d}\gamma_L}{\mathrm{d}C_B}$$
(3.36)

The Gibbs equation in this form can be applied to a non-ionic surfactant or inertelectrolyte solution. For a solution of an ionic surfactant in the absence of any other electrolyte, however, the equation should be modified to

$$\Gamma_B = -\frac{1}{2R_gT}\frac{\mathrm{d}\gamma_L}{\mathrm{d}\ln C_B} = -\frac{C_B}{2R_gT}\frac{\mathrm{d}\gamma_L}{\mathrm{d}C_B}$$
(3.37)

Equations (3.36) and (3.37) can be used for calculating the surface excess concentration in the presence of electrolyte and surfactant solution respectively.

3.6.2 Surfactant adsorption

Somasundaran and co-workers [69] used a modified form of Stern isotherm for low surfactant concentrations to express the adsorption of positive counterions at the plane δ_s given by

$$\Gamma_{\delta}^{+} = 2r_{\delta s}C\exp(-W_{\delta s}/k_{B}T)$$
(3.38)

where $r_{\delta s}$ is the radius of the adsorbed ion at the plane δ_s , C is the concentration of ions per unit volume, and $W_{\delta s}$ is the transfer energy necessary to bring the ion from the bulk of the solution up to the plane δ_s .

The work $W_{\delta s}$ can be divided into electrostatic and chemical energy terms as given in equation (3.39)

$$W_{\delta s} = z_{+}e\varphi_{\delta s} - \phi \qquad (3.39)$$

where ϕ is the van der Waals energy, in the units of k_BT , associated with the removal of the alkyl chain from the liquid and related to an alkyl chain of n_c carbon atoms as $\phi/k_BT = n_c \phi' / k_BT$ where n_c is the number of CH₂ groups in the surfactant molecule and ϕ' is the van der Waals energy of interaction per CH₂ group between the surfactant molecules. Substituting equation (3.39) into equation (3.38), the surface excess concentration is given as :

$$\ln[\Gamma_{\delta s}^{+}/2r_{\delta s}] = \ln C - (z_{+}e\varphi_{\delta s} - n_{c}\varphi')/k_{B}T \qquad (3.40)$$

At the point of zero charge, $\varphi_{\delta s} = \zeta = 0$, equation (3.40) can be written as follows

$$\ln C_0 = -n_c (\phi' / k_B T) - \ln(\Gamma_{\delta s}^+)_0 - \ln(2r_{\delta s})$$
(3.41)

A value for $\phi' / k_B T$ can be obtained from a slope of the relationship between surfactant concentrations at $\zeta = 0$, C_0 , and n_c .

- 3.7 Coagulation and flocculation

Coagulation is taken to mean the process of destabilising suspended particles by the addition of electrolytes to the suspension. Flocculation is usually defined as the process in which particles are agglomerated by collision motion and the hydrodynamics of the dispersion to form a random structure which is three dimensional, loose and porous [70, 71]. However, both terms are occasionally used interchangeably [72]. Collisions between suspended particles in flocculation can be achieved by three separate mechanisms, namely thermal motion (Brownian motion), bulk liquid motion (stirring) and differential settling. When contacts are produced by Brownian motion, the process is called perikinetic flocculation and orthokinetic flocculation is termed for the stirring or settling mechanism.

3.7.1 Intermolecular forces between particles

An understanding of the destabilisation mechanism from a microscopic viewpoint can be derived from the theory of colloid stability by considering the forces between particles and the particle-solution interactions. The DLVO theory of colloid stability was developed independently by Derjaguin and Landau (1941) and Verwey and Overbeek (1948). This theory involved the estimations of two energy terms, the attractive London-van der Waals energy, V_A , and the repulsive electrical double layer energy, V_R , in terms of inter-particle distance. The attractive energy decreases in accordance with a power law, while the repulsive energy decays exponentially with the distance of separation. The repulsive and attractive energies can be combined to form the total energy of interaction as shown in Figure 3.5. This curve shows that the repulsive energy is dominant at certain distances of separation but at closer distances the attractive energy controls and the particles agglomerate. At intermediate distances, the repulsive energy is usually higher than attractive energy, which gives rise to an energy barrier. When the particles collide with each other with sufficient kinetic energy to overcome the energy barrier, the coagulation process will occur and the suspension will be destabilised.

However, the classical DLVO theory was unable to predict the stability of very hydrophilic and very hydrophobic particle suspensions. Thus, the extended DLVO or non-DLVO theory was proposed by including a term of structural energy or hydrophobic energy [73, 74].



Figure 3.5 Total energy of interaction combined from attractive and repulsive energy.

3.7.1.1 Van der Waals forces

Three intermolecular forces, namely dipole orientation (or randomly orienting dipoledipole), induction (or randomly orienting dipole-induced dipole), and dispersion (or fluctuating dipole-induced dipole), are collectively known as van der Waals forces. All interaction energies between atoms or small particles decay as the inverse sixth power of the intermolecular distance. However, the van der Waals-London interactions are important between particles in aqueous media containing electrolytes. According to van Oss [75], Hamaker calculated the van der Waals-London interaction energy for two semi-infinite flat parallel bodies separated by a distance ℓ in air or *in vacuo*, as :

$$V_A = -\frac{A_{ii}}{12\pi\ell^2}$$
(3.42)

where A_{ii} is the Hamaker constant. For material 1 immersed in medium 3, the Hamaker constant is given as :

$$A_{131} = \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)^2 \tag{3.43}$$

For two materials 1 and 2 immersed in medium 3, the Hamaker constant is given as :

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}})$$
(3.44)

where A_{11} , A_{22} , and A_{33} are the Hamaker constants for material 1 and 2 and medium 3, respectively.

It is clear that the van der Waals-London interactions for material 1 in medium 3, V_{131} , are always attractive forces but the interactions for materials 1 and 2 in medium 3, V_{132} , are repulsive when :

$$A_{11} > A_{33} > A_{22}$$
 and $A_{11} < A_{33} < A_{22}$

According to Hunter [76], Hamaker also summarised the interaction of two macrobodies for more complicated geometries such as two spheres, two cylinders, and sphere and half-space shown in Figure 3.6.

According to van Oss [75], Lifshitz showed that the free energy of interaction between two semi-infinite parallel slabs, $\Delta G_{ii}(\ell)$, was related to the Hamaker constant by

$$\Delta G_{ii}(\ell) = -\frac{A_{ii}}{12\pi\ell^2}$$
(3.45)

Two spheres



 $r_1, r_2 >> h$



 $r_1, r_2 << h$

Two cylinders





 $r_1, r_2 << h$

Sphere and half-space





 $r_p << h$

Figure 3.6 Van der Waals-London forces for two spheres, two cylinders and sphere and half-space^{*} [76] (* half-space is a body of infinite extent bounded by a plane surface).

then

Israelachvili related the Hamaker constant to a liquid surface tension by

$$\gamma_{i} = \frac{A_{ii}}{24\pi\ell_{0}^{2}}$$
(3.46)

 $\gamma_{i} = -\frac{1}{2}\Delta G_{ii} \qquad (3.47)$

where ℓ_0 is the separation distance between two semi-infinite slabs and γ_i is the surface tension of substance *i*. However, Israelachvili ignored the Born repulsion in his calculation so that this equation may be used only in the case of nonpolar liquids [75].

Good, van Oss and Chaudhury represented the Lifshitz-van der Waals interactions by combining the van der Waals-Keesom, van der Waals-Debye and van der Waals-London interactions in the terms of free energy as follows :

$$\Delta G_{11}^{LW} = -2\gamma_{1}^{LW}$$
(3.48)

where ΔG_{11}^{LW} is the free energy of cohesion *in vacuo* for the Lifshitz-van der Waals interactions. This is always negative (attractive force).

For two identical materials immersed in a medium (3),

$$\Delta G_{131}^{LW} = -2(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}})^2 \qquad (3.49)$$

where ΔG_{131}^{LW} is the free energy of interaction between the two identical materials. Again this is always negative. For two different materials immersed in a medium (3),

$$\Delta G_{132}^{LW} = -2(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}})(\sqrt{\gamma_2^{LW}} - \sqrt{\gamma_3^{LW}}) \quad (3.50)$$

where ΔG_{132}^{LW} is the free energy of interaction between the two different materials. This is positive when $\gamma_1^{LW} < \gamma_3^{LW} < \gamma_2^{LW}$ or when $\gamma_1^{LW} > \gamma_3^{LW} > \gamma_2^{LW}$.

Thus, the Lifshitz-van der Waals interactions can be related to surface tension parameters, easily obtained from contact angle data, with the Hamaker constant used to calculate van der Waals forces.

3.7.1.2 Double layer interactions

From the Gouy-Chapman model in section 3.4.1, the electrical potential between two charged infinite plates may be described by

$$\frac{\mathrm{d}^2 \varphi}{\mathrm{d}x^2} = \frac{2zen_0}{\varepsilon} \sinh\left[\frac{ze\varphi}{k_B T}\right]$$
(3.51)

According to Hogg and co-workers [77], the potential between two dissimilar infinite plates was described by the Debye-Huckel equation as :

$$\frac{d^2\varphi}{dx^2} = \kappa^2\varphi \tag{3.52}$$

One solution for two dissimilar plates separated by distance 2d has been shown to be:

$$\frac{\varphi}{4\pi} = \varphi_1 \cosh \kappa x + \left(\frac{\varphi_2 - \varphi_1 \cosh 2\kappa d}{\sinh 2\kappa d}\right) \sinh \kappa x \quad (3.53)$$

where φ_1 and φ_2 are the potentials of each plate at x = 0 and x = 2d, respectively.

The potential energy of interaction between the double layers of two parallel flat plates, V_{I} , is equal to the free energy between the double layers and the result shows as:

$$V_{I} = \frac{\varepsilon \kappa}{2} \left[\left(\varphi_{1}^{2} + \varphi_{2}^{2} \right) (1 - \coth 2\kappa d) + 2\varphi_{1} \varphi_{2} \operatorname{cosech} 2\kappa d \right]$$
(3.54)

When this equation was applied to the interaction between two spheres given by r_{p1} and r_{p2} , by Derjaguin's method [76], the constant potential, $V_E^{\varphi-\varphi}$, at both surfaces was given as:

$$V_{E}^{\phi-\phi} = \frac{\pi \varepsilon r_{p1} r_{p2}(\phi_{1}^{2} + \phi_{2}^{2})}{(r_{p1} + r_{p2})} \left\{ \frac{2\phi_{1}\phi_{2}}{(\phi_{1}^{2} + \phi_{2}^{2})} \ln\left(\frac{1 + \exp(-\kappa h)}{1 - \exp(-\kappa h)}\right) + \ln(1 - \exp(-2\kappa h)) \right\} (3.55)$$

where h is the distance between the two spherical particles. The spherical double layer interaction in the case of constant charge [78] was given as:

$$V_{E}^{\sigma-\sigma} = V_{E}^{\phi-\phi} - \frac{4\pi\varepsilon r_{p1}r_{p2}(\phi_{1}^{2}+\phi_{2}^{2})}{(r_{p1}+r_{p2})}\ln(1-\exp(-2\kappa h))$$
(3.56)

3.7.1.3 Non-DLVO theory

Other surface forces, such as hydrophobic, steric polymer adsorption, and fluctuating wave forces [79], have been found in recent years to be important because classic DLVO theory failed to explain some phenomena exhibited by hydrophobic and hydrophilic surfaces. Hydrophobic forces are important forces when surfactants are added into solutions while hydration forces are present when suspensions are treated with coagulants, which are very relevant to flocculation and dissolved air flotation.

Hydrophobic forces were first measured on flat mica surfaces in equilibrium with surfactant solutions and they can be described using experimental equations of an exponential force, a double exponential force and a power law as follows:

$$\frac{F_h}{R} = C_1 \exp\left\{-\frac{h}{D_1}\right\}$$
(3.57)

$$\frac{F_h}{R} = C_1 \exp\left\{-\frac{h}{D_1}\right\} + C_2 \exp\left\{-\frac{h}{D_2}\right\}$$
(3.58)

$$\frac{F_h}{R} = -\frac{K_h}{6h^2} \tag{3.59}$$

where F_h is the hydrophobic forces, h is the closest separation distance between two curved surfaces of curvature R, C_1 and C_2 are exponential constants, and D_1 is the decay lengths in the range of 1-2 nm, D_2 is the decay length in the range of 10-26 nm and K_h is a hydrophobic force constant.

3.7.2 Coagulation and flocculation processes

A combination of four models may be used to explain an agglomeration or destabilisation process. These are double layer compression, adsorption to produce charge neutralisation, entrapment in a precipitate described as sweep flocculation, and a bridging mechanism. However, some of these mechanisms may take place simultaneously. Destabilisation is obtained when the coagulants are added to the suspension. The process involves three steps before separation occurs. In the first step, the chemicals are dispersed initially by rapid mixing and high turbulence. Secondly, the rapid mixing continues to promote the initial flocculation by the collision of the primary particles. Finally, the mixing speed is reduced to allow the small primary flocs to aggregate to form bigger flocs. The last two steps take place usually in the flocculation tank promoting inter-particle contacts. These contacts can occur either by random Brownian motion or by the forced collision due to hydrodynamic forces.

For batch flocculation, a first-order model is assumed to describe the kinetics of aggregation and a zero order relationship used to represent the floc breakup process [39] as shown in equation (3.60)

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -K_A G N + K_B G^{I_B} \tag{3.60}$$

where K_A is the aggregation constant, K_B is the floc breakup coefficient, N is the number of particles at time t, l_B is the floc breakup exponent, and G is the mean velocity gradient given by

$$G = \left(\frac{P_{in}}{V\mu}\right)^{1/2}$$
(3.61)

where P_{in} is the power input to the fluid, V is the liquid volume and μ is viscosity.

In dilute suspensions, flocs are aggregated by intermolecular forces and disaggregated by fluid forces simultaneously. The mechanisms of floc breakup are not exactly known but the general concepts accepted that surface erosion from the flocs and fracture of flocs to form smaller aggregates were the explanation. A stable floc size arising from aggregation and breakup can defined by both models as :

$$d_s = C_s G^{I_B} \tag{3.62}$$

where d_s is the stable floc size, C_s is the floc strength coefficient and l_B is the exponent constant.

3.8 Hydrodynamics of spherical particles

The drag force on a spherical particle, neglecting the inertial force at low Reynolds number, can be determined using the Navier-Stokes' equations and the solution is known as Stokes' law, given by [80]:

$$F_n = 6\pi\mu r_p u_n \tag{3.63}$$

where u_n is the fluid velocity relative to the particle in normal direction.

For a single particle moving onto a collector surface as shown in Figure 3.7, a dimensionless parameter, $H = h/r_p$, was introduced [81] and the velocity of the particle in the normal and tangential directions can be represented by equations (3.64) and (3.65), respectively, as :

$$u_{np} = r_p \frac{\mathrm{d}H}{\mathrm{d}t} = \frac{F_i f_1}{6\pi\mu r_p}$$
(3.64)

and

$$u_{\alpha p} = r_p \frac{\mathrm{d}\alpha}{\mathrm{d}t} = u_\alpha f_3 \tag{3.65}$$

where F_t is the total force, u_{np} is the particle velocity in normal direction, $u_{\alpha p}$ is the particle velocity in tangential direction, u_{α} is the fluid velocity in tangential direction, α is the angular angle between a collector and a particle, f_1 and f_3 are the universal functions for the dimensionless gap width of particle velocity in normal and tangential direction, respectively [82].

The Stokes' law in equation (3.63) can be applied readily when a particle is far from a collector. However, when the particle moves near the collector the normal force is distorted because of a resistance force [83]. This may be explained as due to the fluid between the particle and the collector flowing away as the particle moves to the collector. In comparison to a free body in fluid stream, the stream line around the particle in the case of the particle moving near the collector surface is changed. The normal force in this case may be represented in a modified Stokes' equation as :

$$F_n = 6\pi\mu r_p u_n f_2 \tag{3.66}$$

Theory



Figure 3.7 Particle path moving around a collector.

where f_2 is the universal function of the dimensionless gap width in the normal direction which is a function of particle size, and the distance between particle and collector, h.

For the undisturbed axisymmetric flow field, the Stokes' stream function around a spherical particle is given as :

$$\Psi = -(\frac{A}{r} + Br - \frac{1}{2}ur^2)\sin^2\alpha \qquad (3.67)$$

where *u* is the fluid velocity,
$$A = -\frac{1}{4}ur_p^3$$
 and $B = \frac{3}{4}ur_p$.

In the case of the flow field around a bubble, the stream function may be written as:

$$\Psi = \frac{3}{4}u(r-r_B)^2 \sin^2 \alpha$$
 (3.68)

where $r = r_p + r_B + h$ and the fluid velocities in the normal direction, u_n , and tangential direction, u_{α} , are given as:

$$u_n = -\frac{1}{r^2 \sin \alpha} \frac{\partial \Psi}{\partial \alpha}$$
(3.69)

$$u_{\alpha} = -\frac{1}{r \sin \alpha} \frac{\partial \psi}{\partial r}$$
(3.70)

Substituting equation (3.68) into equation (3.69) and (3.70), the solutions for the normal and tangential velocities of the fluid around a spherical particle can be represented as [81]:

$$u_n = -\frac{3R^2(H+1)^2 u_B \cos\alpha}{2(1+HR+R)^2}$$
(3.71)

and
$$u_{\alpha} = \frac{3R(H+1)u_B \sin \alpha}{2(1+HR+R)}$$
 (3.72)

where $H = h/r_p$, and $R = r_p/r_B$

Equation (3.66) can be used to calculate the hydrodynamic force on a small particle moving to a spherical collector when it is combined with equation (3.64) to (3.72). The basic equations in this section will be used to model the flotation process in the following chapter.

Chapter 4

Flotation models

4.1 Introduction

An understanding of flotation models is a key step in attempts to improve the efficiency of flotation units used to separate particles from liquid. In the flotation process, the models of collision and attachment between particles and bubbles have to describe complicated mechanisms because of the interaction between the three phases in the process. This situation is influenced not only by the surface charges but also by the hydrodynamic interactions around the rising bubbles in the liquid phase. The aim of this chapter is to introduce flotation models including the general concepts of simple and complicated flotation mechanisms.

The flotation models may be classified into simple and complicated models depending on the complexity of the mathematics as shown in Figure 4.1. Early workers observed collision and attachment phenomena between particles and bubbles using a microscope and proposed the simple models, which are also explained by empirical equations. The complicated models may be sub-divided to the single collector collision model, the model based on surface chemistry and hydrodynamic theory and the population balance model.

The single collector collision model was investigated by considering both filtration theory and hydrodynamics, and is summarised using individual terms of efficiency: Brownian diffusion, interception, gravity forces and inertia forces. The model based on surface chemistry and hydrodynamic theory was developed by considering both hydrodynamics and surface chemistry, expressed in the function of three terms of probability: bubble-particle collision, adhesion and surface energy, and detachment. Finally, the population balance model described a process of bubble-floc collision and attachment in a mixing zone and a rising velocity of agglomerates in a flotation tank.



Figure 4.1 A classification of flotation models.

For the bubble-particle collision, the trajectories of a bubble and a particle were generally described by using the stream function for fluid around a spherical collector. The attachment was represented in terms of the kinetic energy of a particle approaching a bubble and detachment defined as occurring when the kinetic energy that tears the particle off the bubble surface is higher than the sum of the work of adhesion and the energy barrier. However, many investigators [60, 81] normally neglected this parameter in their models. Finally, the adhesion and surface energy were reported in the terms of the DLVO theory and non-DLVO theory including electrostatic, van der Waals and hydrophobic energies.

4.2 Simple models

In 1960, Vrablik [84] proposed three different ways that flotation may be achieved: the adhesion of a gas bubble to a suspended solid, the trapping of gas bubbles in a floc structure as the gas bubbles rise, and the adsorption of gas bubbles in a floc structure as the floc is formed, as shown in Figure 4.2. Recently, however, another collision model was proposed that is due to turbulence induced in the suspension [59].



Figure 4.2 Three flotation models proposed by Vrablik [84] (a) adhesion of a gas bubble to a suspended solid (b) trapping of gas bubbles in a floc structure as the gas bubbles rise and (c) the adsorption of the gas bubbles in a floc structure as the floc is formed.

In dissolved-air flotation with recycle pressurisation, both the bubble formation and entrapment mechanisms are less important than the collision stages because the normal practice of bubble production is to release clean saturated water from an air saturator so supersaturated water is not added directly to the suspension. Although there is some small degree of supersaturation, it seems to be negligible.

In the different process of dispersed air flotation Jameson and co-workers [85] described the collision and attachment models as a series of stages. Firstly, the collision stage; when the particles and the bubbles flow into the flotation cell, they have a chance to move on the same trajectories so that the particles and bubbles come close together. Secondly, the film-thinning stage, when the gap between the particles and the bubbles is small, the liquid between them will form a film. The viscous stresses in this thin film become high, which reduces the approach velocity between the particle and the bubble. For a hydrophobic surface, the molecular forces, wetting or disjoining pressures, are responsible for the rupture of the liquid film. Finally, in the film recession stage, the liquid around the point of rupture or initial coalescence between the particle. In this stage, if the conditions in the flotation cell are highly turbulent, it is possible for particles to be dragged off the surface of the bubbles and to be swept into the liquid by viscous stresses or turbulent eddies.

In 1948, Sutherland proposed that the overall rate of flotation was equal to the product of three factors, namely the rate of collision between particles and bubbles, the probability of adhesion after collision, and the probability of detachment. To find the rate of collision between a single particle and a bubble, the flow around the bubble was assumed to be inviscid and had no effect on the streamlines around the bubble. The collision efficiency was defined as:

$$\eta_c = \left(\frac{r_c}{r_b}\right)^2 = \frac{3r_p}{r_b}$$
(4.1)

where η_c is the collision efficiency, r_c is the critical radius, r_b is the bubble radius and r_p is the particle radius.

The total removal rate was represented by a first order kinetic equation as:

$$-\frac{dN_{t}}{dt} = (\pi r_{c}^{2} H_{t} N_{p}) \frac{Q_{g}}{\frac{4}{3} \pi r_{b}^{3}} = \left(\frac{9r_{p} H_{t} Q_{g}}{4r_{b}}\right) N_{p}$$
(4.2)

where N_t is the total number of particles in the flotation cell, N_p is the number of particles per unit volume, t is time, H_t is the liquid depth in the flotation cell and Q_g is the flow rate of gas in the flotation cell.

Reay and Ratcliff [86] pointed out that particles larger than 3 μ m approximately will not be affected by Brownian motion. The collection efficiency η_{Tc} of the bubble, defined as the fraction of particles in the bubble path which are actually picked up by the bubble, increased with increasing particle diameter as shown in equation (4.3)

$$\eta_{Tc} = \eta_c \eta_a \tag{4.3}$$

where η_a is the attachment efficiency depending on the chemical nature of particle and bubble surfaces and the thin film of liquid draining from between them. η_c is the collision efficiency and it is the function of particle and bubble size. For sub-micron particles, the collection efficiency was controlled by diffusion and the flotation rate shown to be inversely proportional to $d_p^{2/3}$. The flotation of sub-micron particles was also improved substantially when big flocs were formed.

In 1977, Collins and Jameson [13] also assumed that the rate of removal of particles from the flotation cell was first-order with respect to the particle concentration. In a batch flotation process, the rate of removal of particles from the flotation cell can be and

described in terms of the total number of particles removal by a bubble as it rises, through the liquid of height, H_t , in equation (4.4)

$$-\frac{\mathrm{d}N_{i}}{\mathrm{d}t} = \left(\frac{3Q_{g}E_{c}H_{i}}{2d_{b}V_{c}}\right)N_{i} \qquad (4.4)$$

$$k_{1} = \left(\frac{3Q_{g}E_{c}H_{i}}{2d_{b}V_{c}}\right)$$

where E_c is the collection efficiency, V_c is the total volume of the flotation cell and d_b is the bubble diameter.

Collins and Jameson also proposed that an empirical equation for the rate constant depended on particle diameter and the electromobilities of the particle and the bubble given as

$$-\ln(\frac{k_1}{d_p^{1.5}}) = 3.9 + 0.116U_E U_B$$
(4.5)

where d_p is the particle diameter, U_E is the electromobility of the particle and U_B is the electromobility of the bubble.

The simple models described in this section use only concepts of bubble and particle attachment and empirical equations for the flotation rate. A first order kinetic equation was used to describe the results of experiments and Collins and Jameson included the electrostatic force in the model as an empirical equation. However, the other forces such as the van der Waals and hydrophobic forces will be introduced in the next section.

4.3 Single collector collision model

According to Ward [60], the overall single collection mechanism may contain interception, gravity and Brownian diffusion mechanisms. The total single-collector

collision efficiency, defined as a ratio of particle-bubble collision rate to particlebubble approach rate, is the sum of individual terms of efficiency as given in equation (4.6)

$$\eta_T = \eta_d + \eta_i + \eta_g \tag{4.6}$$

$$\eta_d = 6.18 \left(\frac{k_B T}{g \rho_w}\right)^{2/3} \left(\frac{1}{d_p}\right)^{2/3} \left(\frac{1}{d_b}\right)^2$$
(4.7)

$$\eta_i = 3/2 \left(\frac{d_p}{d_b}\right)^2 \tag{4.8}$$

$$\eta_g = \left(\frac{\rho_p - \rho_w}{\rho_w}\right) \left(\frac{d_p}{d_b}\right)^2$$
(4.9)

where η_T is the total single-collector collision efficiency, η_d is the Brownian diffusion efficiency, η_i is the interception efficiency, η_g is the efficiency of the gravity force, k_B is Boltzmann constant, ρ_w is the water density and ρ_p is the particle density.

The results showed that a diffusion mechanism is dominant when particle sizes are smaller than 1 μ m. On the other hand, an interception mechanism is the controlling step when the particle sizes become bigger. η_T is controlled by an interception mechanism when the floc is bigger than 5 μ m. When the bubble diameter is about 40 μ m and the floc diameter bigger than 32 μ m, equation (4.6) shows that the value of η_T is nearly one.

Malley and co-workers [87, 88] used the concept of the single-collector collision efficiency to analyse the flotation kinetics but also included inertia effects. However,

the inertia efficiency can be negligible in dissolved air flotation because the inertia force is not significant for bubble and particle diameters less than $100 \ \mu m$ [49].

The particle removal rate was given as

$$\frac{\mathrm{d}N_p}{\mathrm{d}H_t} = -\left(\frac{3\eta_a\eta_T\Phi N_p}{2d_b}\right) \tag{4.10}$$

where H_t is the tank depth, η_a is the attachment efficiency and Φ is the bubble volume concentration.

The overall particle removal efficiency was

$$1 - \frac{N_p}{N_{p0}} = 1 - \exp\left\{-\left(\frac{3\eta_a\eta_T\Phi N_p}{2d_b}\right)\right\}$$
(4.11)

This model requires a measure of the attachment efficiency, usually given by fitting experimental data to the kinetic equation. However, the model provides a good fit to experiments for a system in which surface forces are not dominant.

4.4 Models based on surface chemistry and hydrodynamics

Two groups of researchers i.e. Okada and co-workers [81] and Yoon and co-workers [74, 83] developed flotation models based on surface chemistry and the hydrodynamics of a bubble and particle. Okada and co-workers included the surface forces with the equation of motion of the particle around the bubble and calculated a flotation efficiency by determining a limiting trajectory, named as the trajectory model. On the other hand, Yoon and co-workers determined the flotation efficiency in terms of an overall collection probability given by the probabilities of bubble-particle collision, adhesion and detachment.

Okada and co-workers [81] used the following assumptions:

- As the bubble diameter is small, the rise of the bubble in the solution is represented by Stokes' law (Re < 1).
- As the bubble diameter is much larger than the particle diameter, the bubble is regarded as a locally flat surface.
- 3) The bubble surface is rigid due to the adsorption of surfactant.
- The Brownian motion of the particles and the effect of the adhesion of the particle to the bubble surface by gravity are ignored.

From Figure 3.7 in Chapter 3, the velocities of the particle in the normal and tangential directions to the bubble surface were shown as follows:

$$u_{np} = r_p \frac{\mathrm{d}H}{\mathrm{d}t} = \frac{F_t f_1}{6\pi\mu r_n} \tag{3.64}$$

$$u_{\alpha p} = r_p \frac{\mathrm{d}\alpha}{\mathrm{d}t} = u_\alpha f_3 \tag{3.65}$$

where F_t , is the total force but Okada and co-workers [81] excluded the hydrophobic force for their calculations as given by:

$$F_t = F_e + F_v + F_n \tag{4.12}$$

where F_e is the electrostatic force acting between the bubble and the particle, F_v is the van der Waals force acting between the bubble and the particle and F_n is the normal component of hydrodynamic force acting on the particle.

From the velocity of fluid flow past a sphere in equation (3.71), the normal hydrodynamic force is given as:

$$u_n = -\frac{1}{r^2 \sin \alpha} \frac{\partial \Psi}{\partial \alpha} = -\frac{3R^2(H+1)^2 u_B \cos \alpha}{2(1+HR+R)^2} \quad (3.71)$$

$$F_n = -\frac{3R^2(H+1)^2}{2(1+HR+R)^2} 6\pi\mu r_p u_B f_2 \cos\alpha \qquad (4.13)$$

The equation of motion of the particle moving to the bubble surface is represented as:

$$\frac{dH}{dt} = \frac{F_{t}f_{1}}{6\pi\mu r_{p}^{2}} = \frac{f_{1}}{6\pi\mu r_{p}^{2}} \left\{ -\frac{A_{H}}{6r_{p}H^{2}} + \pi\varepsilon r_{p}\kappa\zeta_{p}\zeta_{b} \left[\frac{4\exp(-\kappa r_{p}H)}{\{1 + \exp(-\kappa r_{p}H)\}} \right] -\frac{3R^{2}(H+1)^{2}}{2(1 + HR + R)^{2}} 6\pi\mu r_{p}u_{B}f_{2}\cos\alpha \right\}$$
(4.14)

From the tangential velocity, u_{α} , of fluid around the bubble given in equation (3.72), the equation of motion of the particle tangential to the bubble surface is represented as:

$$u_{\alpha} = \frac{1}{r \sin \alpha} \frac{\partial \psi}{\partial r} = \frac{3R(H+1)u_B \sin \alpha}{2(1+HR+R)}$$
(3.72)

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = \frac{3R(H+1)u_B f_3 \sin\alpha}{2r_b (1+HR+R)^2}$$
(4.15)

By combining equations (4.15) and (4.14), the final result is given by:

$$\frac{dH}{d\alpha} = \frac{f_1}{6\pi\mu r_p^2} \frac{2(1+HR+R)^2}{3R^2(H+1)u_B f_3 \sin\alpha} \left\{ -\frac{A_H}{6r_p H^2} + \pi\varepsilon r_p \kappa \zeta_p \zeta_b \right\} \\ \left[\frac{4\exp(-\kappa r_p H)}{\left\{ 1+\exp(-\kappa r_p H) \right\}} \right] - \frac{3R^2(H+1)^2}{2(1+HR+R)^2} 6\pi\mu r_p u_B f_2 \cos\alpha \left\}$$
(4.16)

This equation can be solved for the limiting trajectory, l_L , by numerical methods such as the Runge Kutta technique and a particle capture efficiency per bubble, η_{Tc} , is then calculated by:

$$\eta_{Tc} = (l_L / r_b)^2$$
 (4.17)

When the detachment efficiency is neglected, the particle capture efficiency is equal to $\eta_c \eta_a$ and the flotation efficiency can be determined by equation (3.8) for the batch process and equation (3.9) for the continuous flotation process.

$$1 - \frac{N_p}{N_{p0}} = 1 - \exp\{(-\eta_c \eta_a)(A_b N_b)H_c\}$$
(3.8)

$$1 - \frac{N_p}{N_{p0}} = 1 - \exp\{(-\eta_c \eta_a)(A_b u_b N_b)\tau\}$$
(3.9)

Yoon and Mao [74] represented flotation by a first order kinetic equation as :

$$\frac{\mathrm{d}N}{\mathrm{d}t} = -\left(\frac{3\eta_R}{4r_b}V_g\right)N = -k_PN \qquad (4.18)$$

where η_R is the collection probability, V_g is the superficial velocity of air defined as a volumetric air flow rate normalised by the cross-sectional area of a flotation column and k_P is the collection kinetic constant.

According to Luttrell and Yoon [82], the probability, η_R , of a particle collected by an air bubble during flotation may be shown as:

$$\eta_R = \eta_c \eta_a (1 - \eta_{da}) \tag{4.19}$$

where η_c is the probability of bubble-particle collision, η_a is the probability of adhesion and η_{da} is the probability of detachment.
The simplest models for predicting η_c are based on calculating the volume swept by a bubble in a flotation cell under quiescent conditions [82, 89, 90]. The results of hydrodynamic models may be summarised in equation (4.20)

$$\eta_c = A_1 \left(\frac{d_p}{d_b}\right)^{n_p}$$
(4.20)

where A_1 is an empirical constant which is a function of the Reynolds number of the bubble and n_p is the power index constant normally given as 2 for the bubbles used in flotation.

However, some investigators [74, 82] represented η_c in the forms as follows:

$$\eta_c = \left(\frac{r_c}{r_p + r_b}\right)^2 \tag{4.21}$$

and

$$\eta_{c} = \left[\frac{3}{2} + \frac{4 \operatorname{Re}^{0.72}}{15}\right] \left(\frac{r_{p}}{r_{b}}\right)^{2}$$
(4.22)

where r_c is the critical radius, Re is Reynolds' number of the bubble, r_b is the bubble radius and r_p is the particle radius.

The probability of bubble-particle adhesion η_a and the probability of bubble-particle detachment η_{da} could be given as equation (4.23) and (4.24) respectively.

$$\eta_a = \exp\left(-\frac{E_1}{E_k}\right) \tag{4.23}$$

$$\eta_{da} = \exp\left(-\frac{W_a + E_1}{E'_k}\right) \tag{4.24}$$

where E_1 is the energy barrier, E_k is the kinetic energy of the particles, W_a is the sum of the work of adhesion and E'_k is the kinetic energy of detachment that tears the particles off the surface.

The DLVO theory may be described by a curve of total energy, V_{t} , against bubbleparticle distance, h, as shown in Figure 4.3. The energy barrier, E_1 , occurs at h_1 and a secondary energy minimum, E_2 , shows at h_2 . If the kinetic energies, E_k , of particles are smaller than E_1 or E_2 , coagulation may occur with an equilibrium interparticle distance at h_2 . If the kinetic energies of particles are larger than E_1 , coagulation will occur at a distance smaller than h_1 referred to as a critical rupture thickness. Thus, the necessary condition for bubble particle adhesion is $E_k \ge E_1$, and the probability of bubble particle adhesion can be represented as equation (4.23).

The details of the kinetic energies of the particles and detachment, the energy barrier and the work of adhesion can be found in Yoon and co-workers [74, 91, 92].



Figure 4.3 A curve of V_1 against h using DLVO theory shows the energy barrier E_1 at h_1 and a secondary energy minimum E_2 at h_2 .

4.5 Population balance model

The volume of a flotation tank may be considered to consist of two zones i.e. a contact zone and a separation zone. In the contact zone, a flocculated suspension is mixed with pressurised water to produce bubble-floc agglomerates. After a collisionattachment between air bubbles and flocs, the agglomerates rise to the tank surface in the separation zone. Turbulent flow is generally produced by mixing of the two streams in the contact zone while laminar flow is required in the separation zone.

For the population balance model [93-95] two cases are considered i.e. a floc particle larger than an air bubble $(d_f > d_b)$ and a floc particle smaller than an air bubble $(d_f < d_b)$.

Case 1, $(d_f > d_b)$, and the number of air bubbles attached to a floc particle is large: a drag force acting on the agglomerates produced from *i* bubbles attached to a floc can be represented as:

$$\frac{\pi}{6}i(\rho_{w}-\rho_{b})gd_{b}^{3}-\frac{\pi}{6}(\rho_{f}-\rho_{w})gd_{f}^{3} = F_{D} \qquad (4.36)$$

where F_D is the drag force and d_f is the floc diameter.

Since $\rho_w \gg \rho_b$ and the buoyancy force of air bubbles attached to a floc should be much larger than the apparent gravity force of a floc particle in water, then the drag force is given as:

$$\frac{\pi}{6}i\rho_w gd_b^3 = F_D \tag{4.37}$$

If a bubble-floc agglomerate is assumed to be a solid particle, the drag force is written as:

$$F_D = 3\pi\mu d_{fb} v \varphi_{sh}^{-1/2}$$
(4.38)

and
$$d_{fb} = \left(id_b^3 + d_f^3\right)^{1/3}$$
 (4.39)

where φ_{sh} is the sphericity of the bubble-floc agglomerate and d_{fb} is the diameter of the agglomerate.

Substituting equations (4.38) and (4.39) into equation (4.37), the rising velocity of the agglomerate is represented as:

$$w_{dj} = \frac{ig\rho_w d_b^3}{18\mu(id_b^3 + d_f^3)^{1/3}} \varphi_{sh}^{1/2}$$
(4.40)

Case 2, $(d_f < d_b)$, and the number of particles attached to an air bubble is large: the rising velocity of an agglomerate produced from *j* particles attached to a bubble is represented as:

$$w_{d,i} = \frac{g\rho_w d_b^3}{18\mu (d_b^3 + jd_f^3)^{1/3}} \varphi_{sh}^{1/2}$$
(4.41)

Matsui and co-workers [93, 94], represented the rate of flotation as:

$$\frac{\mathrm{d}N_p}{\mathrm{d}t} = -k_1 N_p N_b \eta_a \tag{4.42}$$

where k_1 is the rate constant, N_p is the number concentration of particles, N_b is the number concentration of bubbles and η_a is the attachment efficiency.

Since the collisions between bubbles and agglomerates in the mixing zone occur by turbulent and gravitational motions, the rate constant may obtain as:

$$k_1 = \sqrt{k_T^2 + k_G^2}$$
 (4.43)

$$k_T = a_1 \sqrt{\frac{P_{in}}{\mu V}} (d_b + d_p)^3$$
 (4.44)

and
$$k_G = \frac{1}{36} \sqrt{\frac{2\pi}{3}} \rho_w d_b^2 (d_b + d_p)^2 \frac{g}{\mu}$$
 (4.45)

where k_T is the collision rate coefficient related to turbulent fluid motion, k_G is the collision rate coefficient related to gravitational motion, a_1 is the coefficient (= 0.385 according to Tambo and co-workers and = 0.209 according to Saffman and Turner; however, the coefficient will be discussed again in Chapter 9) and P_{in} is the energy dissipation per unit volume of fluid. However, if good mixing in the contact zone is assumed, the collision rate will be controlled by turbulent motion. Then,

$$k_1 \simeq k_T$$
 (4.46)

Attachment efficiencies in the model presented by Matsui and co-workers [93, 94] are the function of the number of attached bubbles in case 1 ($d_f > d_b$) and the function of the number of attached particles in case 2 ($d_f < d_b$). However, it seems that it is difficult to evaluate the attachment efficiency and thus to determine a flotation efficiency. Following Matsui and co-workers' concept, the population balance model will be developed further in Chapter 9 as a mixing zone model by introducing surface chemistry effects to describe the attachment efficiency.

4.6 Summary

The flotation models may be divided to the single collector collision model, the model based on hydrodynamics and surface chemistry, and the population balance model. The advantage of the model based on hydrodynamics and surface chemistry is that a good prediction can be obtained and the model is not too complicated to solve by a numerical method. Clearly, the interfacial forces are the controlling parameters in describing the attachment efficiency aspect of flotation.

Chapter 5

Experiments

The experimental work in this study may be divided into flocculation, zeta potential and contact angle measurements, floc strength testing and flotation experiments on a pilot scale. Coagulation and flocculation were performed using a flocculation bench based on the WRC design [96]. Zeta potential measurements were made on both bubbles and clay particles. A test on bubbles involved measuring the charge on a single bubble in a cationic surfactant solution using the microelectrophoresis method introduced by Collins and co-workers [14]. Zeta potentials of clay particles were measured and related to coagulation data to obtain the optimum conditions for the removal of fine particles from water. To determine other surface forces, the contact angles of polar and non-polar liquids on a variety of flat clay surfaces were obtained by a technique using a sessile drop of the liquid. Finally, a semicontinuous flotation process was operated at a suspension flow rate of 2 L/min under various conditions and the results were compared with flotation models as described in Chapter 9.

5.1 Materials

5.1.1 Clays

Both kaolin and Wyoming bentonite were used for all experiments. Samples of these had been analysed previously by the Natural History Museum [97]. The results showed both clays to be very pure i.e. 90 % for kaolin and 93% for Wyoming bentonite. The cation exchange capacity, CEC, of the kaolin was 12.5 meq/100 g and 63.1 meq/100 g for the Wyoming bentonite, suggesting that Wyoming bentonite suspensions require a high concentration of ions to produce surface saturation.

5.1.2 Surfactants

Three cationic surfactants of the alkyl-trimethylammonium bromide family with different chain lengths namely, dodecyltrimethylammonium bromide, $C_{15}H_{34}NBr$ (MW 308.3), tetradecyl-trimethylammonium bromide, $C_{17}H_{38}NBr$ (MW 336.4), and hexadecyltrimethylammonium bromide, $C_{19}H_{42}NBr$ (MW 364.5), and an anionic surfactant, sodium dodecyl sulphate, $C_{12}H_{25}O_4SNa$ (MW 288.4), were used. All surfactants were of analytical grade quality and were obtained from Sigma-Aldrich Company Ltd., UK.

5.1.3 Coagulants

Three common coagulants, alum, $Al_2(SO_4)_3.16H_2O$, ferric chloride, FeCl₃ (anhydrous), and polyaluminium chloride, PAC, were used in commercial grade form. The aluminium sulphate and ferric chloride were obtained from Fisons Ltd., UK and the PAC from Laporte Industries Ltd., UK. Alum and ferric chloride were supplied in powder form, while PAC was obtained in 10% wt/wt solution.

5.1.4 Other chemicals

For the contact angle measurements, diiodomethane (CH_2I_2) , glycerol $(C_3H_8O_3)$, and 1-bromonapthalene $(C_{10}H_7Br)$ were obtained from Acros, Geel, Belgium. These chemicals were analytical grade with 99+% for diiodomethane and glycerol and 96+% for 1-bromonapthalene, respectively.

5.2 Apparatus

5.2.1 Flocculation bench

The flocculation bench consists of six stirrers, 4-paddle blade turbine type, connected to a constant torque motor and an automated control box. Each agitator is 50 mm in

diameter with a blade area of 15×15 mm and made from stainless steel as shown in Figure 5.1. A sequence of mixing times and stirrer speeds was automatically controlled (see details in Reference [96]).

5.2.2 Zeta potential equipment

Two different apparatuses based on electrophoresis were used for the measurement of zeta potentials i.e. one by Rank Brothers, Cambridge, UK, for the measurements of zeta potential of bubbles and a Malvern Zetamaster, Malvern Instruments Ltd., UK, for the clay suspensions.

The Rank Brothers' equipment was operated by applying a DC current across a glass cell, filled with electrolyte, to induce the charged particles into moving with constant velocity. A video camera system was used to note the particle velocities and zeta potentials were calculated by Smoluchowski's equation [67]. For these experiments, the rectangular cell, internal dimensions 0.8 x 10 x 40 mm, was modified by drilling two small holes at the top and bottom of the cell. A platinum wire was fixed into the small holes with silicone rubber sealant. The platinum wires were connected to a variable voltage power supply and the bottom wire was fixed to earth as shown in Figure 5.2 so that the bubble was not charged by the circuit. This technique, introduced by Collins and co-workers [14], was used to create the gas bubbles in the cell of about 30 µm diameter which is the same order of magnitude as the size of the bubbles used in the flotation tests. Figure 5.3 illustrates the Rank Brothers' microelectrophoresis apparatus, consisting of an equipment controller with water bath, a rectangular cell, a DC power supply, a monitor and a video recorder.

The Malvern Zetamaster is an automated machine using a light scattering technique and the Doppler effect, where the light is shifted in frequency when the particles are moving, to make the electromobility measurements. The two incident laser beams of equal intensity meet each other at a stationary level and form an interference pattern. The particles, moving under the action of applied electrical potential, give rise to pulses of scattered light when passing through the bright fringes. The time interval between two consecutive pulses is measured. Then, the particle velocity is obtained from the distance between the bright fringes divided by the time interval. This technique gives more reliable results than the Rank Brothers' method because of the larger number of particles examined (about 4000 particles per measurement). Figure 5.4 pictures the quartz cell connected to a sample injection point and the equipment controlled using a PC computer with the Zetamaster software.

5.2.3 Turbidimeter

The turbidity of the samples and effluents was measured using a Hach model 16800 apparatus made by Camlab, UK. Each measurement was calibrated against a universal formazine standard in Nephelometric Turbidity Units, NTU, and used distilled water as a reference.

5.2.4 Contact angle tester

The contact angles on flat surfaces were measured using a model G40 apparatus made by Kruss, Hamburg, Germany. A drop of liquid was placed using a microsyringe on the surface of clay discs and the advancing contact angle was measured visually through a microscope objective. The microsyringe needle was fixed above the tested surface and the drop of liquid was enlarged by injecting more liquid during measurement. This technique had the advantage of eliminating the sedimentation effect [98]. The contact angle measurement was repeated at least five times. The reproducibility error was ± 2 degrees.

5.2.5 Particle size analysis

The size distributions of the particles in the suspensions were measured using a Lasentec model A100 apparatus by Lasentec Inc., Redmond, USA. This equipment operates by scanning a high intensity laser beam over the particles at its focus point

and measures the time duration of the back scattered pulses of light. Figure 5.5 shows the Lasentec probe connected to a stirred tank. The external dimensions of the probe are 25.4 mm diameter and 317.5 mm length. Before using this equipment, the window of the probe was carefully cleaned until the particle counts were less than 100 counts and the differential strength was less than 10 units. This apparatus can measure particle sizes in the range of $0.8-1000 \ \mu\text{m}$. One advantage of the method is that it is less influenced by the colour and reflectivity of the particles or the absorption of the suspending liquid because it determines the time duration rather than the pulse intensity response [47].

5.2.6 Stirred tank reactor

This apparatus was constructed to examine the effect of shear rate on the suspensions. It is shown in the photograph (Figure 5.6). Torque measuring was simply conducted by Newton's third principle [99]. A motor was mounted on a bearing supported on a wooden board above the agitated tank. After switching on the motor, a mechanical force was transmitted through the drive shaft to the motor connected to a lever arm. This reactive torque was measured by transmitting the force through a string linked to a platform scale. The cylindrical reactor made from acrylic plastic was 150 mm diameter and 200 mm height. Two holes were drilled in the reactor at 5 mm and 150 mm from the base and fitted with side tappings made from 8 mm internal diameter acrylic tubes for suspension recirculation by a peristaltic pump. A stainless steel paddle stirrer of 50 mm diameter and 10 mm width was used in the standard tank configuration.

5.2.7 Flotation rig

The flotation rig consisted of a flotation column connected to an air saturator and flocculation tank through a peristaltic pump as shown in Figure 5.7. The details and design calculation are given in Appendix F.

The flotation column, made from acrylic tubing, was 80 mm diameter and 3 metres high. It was fitted with five side taps, made from acrylic rod sleeved internally with 6 mm diameter stainless steel tube, situated along the column every 500 mm. The column was placed on a base plate drilled with two nozzles 6 and 8 mm diameter and situated at the centre and at 30 mm radius respectively. The centre nozzle was connected to the air saturator through a flowmeter and a needle valve, while the other was attached by flexible tubing to the peristaltic pump feeding suspension from the flocculation tank. The top of the column was linked to a rectangular tank, 200 x 400 x 100 mm, arranged to give two zones, a separating and collecting zone, by an acrylic weir. The end of the column was glued to the separating zone, 200 x 360 x 10 mm, allowing floated solids to move to the top of the liquid and to collect in the further zone, 200 x 40 x 100 mm, used as a sludge reservoir. The clear liquid passed out of the separating zone at the far base of this channel by a discharge pipe adjustable in height to act as a weir.

The air saturator, made from stainless steel, was 100 mm diameter and 1100 mm high, consisted of a sparger and metal packing placed on a circular screen at 300 mm height from the bottom of the saturator [97]. At the top of the saturator was the water inlet and air inlet, pressure gauge and safety pressure device. The maximum pressure of this saturator was designed to be 10 barg.

5.3 Sample and chemical preparations

5.3.1 Preparation of clay suspensions

The clay suspensions were prepared by mixing 25 g of dry powder into 800 ml of distilled water. The suspensions were stirred overnight using a magnetic stirrer and were dispersed for 15 minutes using an ultrasonic probe at an output rating of 80 watts. These suspensions were used for DAF testing on the pilot scale. For the

laboratory scale work, the stock clay suspensions were diluted to 10 g/L with distilled water before diluting to the final concentrations with tap water.

5.3.2 Clay surfaces for contact angle measurements

The discs of clay described by Kessaissia and co-workers [100] were prepared by the compression of clay particles. Flocs were produced using the flocculation bench from 50 mg/L clay suspensions with various surfactant and coagulant concentrations. The flocculated samples were filtered and dried at room temperature overnight. The samples were ground in a mortar and were dried at 60°C in an oven overnight. After cooling them in a desiccator, the dried samples were pressed under a 10 ton load using an evacuated die.

5.3.3 Solutions for zeta potential measurements

The surfactants or electrolytes, used in the measurements of zeta potential of bubbles, were diluted to give the requisite concentration with Milli-Q water, which is saturated by introducing oxygen gas into a pressure vessel filled with water and left standing overnight under an internal pressure kept at a constant 0.25 MPa.

Samples used in the measurements of the zeta potential of clay suspensions were prepared using the flocculation bench in the manner described in section 5.4.1.

5.4 Experimental procedure

5.4.1 Flocculation

Each suspension was prepared in a one litre capacity beaker. The mixing sequence on the flocculation bench was set to 100 rpm for 2 minutes and 30 rpm for 20 minutes according to the WRC recommendations [101]. After mixing, the suspensions were

allowed to stand for 15 minutes before taking a sample at a point 10 mm under the liquid surface to measure turbidity.

5.4.2 Rank Brothers' apparatus

After filling the modified rectangular cell with sample, prepared as described in section 5.3.3, and fitting the electrodes, the internal cell height (l_c) and the internal path length (d_c) were measured at $25 \pm 0.5^{\circ}$ C by moving the upper and lower micrometers respectively. The stationary levels were calculated from the Komagata equation (5.1).

$$\frac{s}{d_c} = 0.5 - \left[0.0833 + \frac{32d_c}{\pi^5 l_c} \right]^{1/2}$$
(5.1)

where



The near stationary level was brought into focus by adjusting the lower micrometer.

By applying a pulse of current for approximately 5-10 seconds to the electrolytic cell at constant voltage, bubbles were generated from the lower platinum wire and moved to the upper part of the cell. A bubble in focus was observed on the monitor and the upper micrometer was moved upwards by hand to note the bubble travelling between the marked positions. The position of the mark level relative to the vertical wall was approximately constant within \pm 0.15 cm of the centre of the cell [14]. The motion of bubbles was recorded on a video recorder and the track of those that moved for more than 3 seconds was analysed frame by frame by using a PC fitted with a capture image card. Horizontal velocities for about 20 bubbles were noted by using a graphic programme, such as Coreldraw, and the mean and standard deviation of the zeta potential were calculated by Smoluchowski's equation.

5.4.3 Zetamaster

The samples were prepared using the flocculation bench. A 20 ml volume of suspension was taken using a syringe at about 10 mm depth below the liquid surface and was injected into the apparatus. Five measurements were made on each injection (2-3 injections) and used to calculate an average zeta potential.

5.4.4 Floc strength testing

The stirred tank reactor was filled with clay suspension and set at the standard configuration before moving the Lasentec probe into the reactor and mounting it at 10 degree angle and 30 mm height from the paddle. The distance between the probe and the paddle was as recommended by Peng and Williams [47]. The speed of the motor was regulated at 200 rpm, measured using a tachometer (model TM-3011, RS Company, UK) for few minutes before adding the chemicals. After chemical addition which took 2 minutes, the motor speed was adjusted to the requisite value and the floc size distribution was measured automatically every 10 seconds. The data taken in the last 10 minutes were used to calculate an average value for each test.

5.4.5 Flotation testing

A 500 litre batch of 50 mg/L of clay suspension was prepared in the 1000 litre capacity flocculation tank for each run by the dilution of a stock clay suspension prepared as described in section 5.3.1. The speed of the agitator was regulated to 20 rpm before adding the chemicals. The chemicals were added to the tank over a 3 minute period and mixing was performed for 2 minutes. The agitator speed was reduced to 6 rpm and was maintained at that level until the end of each test. After 20 minutes for slow mixing, the suspension and saturated water were fed into the column and effluent samples were taken every 10 minute to analyse removal efficiencies.

Saturated water was prepared using the air saturator connected to a high pressure liquid pump and an air compressor. The high pressure pump was fed from a water tank supplied with tap water through a floating valve. The air compressor was connected to the air saturator through a regulator and check valve to prevent the liquid flowing back from the air saturator to the air compressor tank. Figure 5.8 shows a flow diagram of the air saturator. The height of liquid in the air saturator was controlled by manual operation to be 300 mm above the base (see details of air saturator in section 5.2.7). The flow rate of saturated water was read from the rotameter placed upstream of the needle valve. The operating pressure was 6 barg and, by varying the flow rate of saturated liquid, the recycle ratio could be adjusted in the range from 6 to 40 %.

5.4.6 Suspended solids testing

A 500 ml sample of suspension was filtered using a 0.2 μ m pore size cellulose nitrate membrane dried at 75° C overnight and cooled in a desiccator. The cake was dried at 75° C in an oven at least 24 hr before cooling in the desiccator. The dried solids of the feed suspension and effluent were used for the calculation of a suspended solid removal efficiency.

5.5 Summary

The DAF rig used a flocculator and a flotation column, which could operate for 4-5 hr at 2 L/min of suspension flowrate. The recycle ratio was varied in the range of 6-40 % by using tap water supplied through the air saturator held at a constant 6 barg for every run. The hydraulic loading rate was 1.5 m/hr and the retention time could be held in the range of 10-30 min but 10 min was normally used. The flotation efficiency was calculated by using turbidity data measured on suspension and effluent samples every 10 min. For floc strength testing, the floc size was measured on-line

using the Lasentec apparatus in a range of shear gradients from 60-265 s⁻¹ in the standard stirred tank rig. For the surface force determination, the advancing contact angle was measured on the flat surface of clay formed from flocs dried and compressed under a 10 ton load. Polar and nonpolar liquids, namely, water, glycerol, diiodomethane and 1-bromonapthalene, were used. Zeta potential measurements on the clay suspensions were performed using the Zetamaster while the zeta potentials of bubbles were determined from bubble mobilities measured using the modified rectangular cell in the Rank Brothers' apparatus. All analytical instruments used in the experiments were commercially available, while the rigs based on the standard designs were constructed by experienced technicians.

All analytical testing and process operations were performed carefully but there were some uncontrollable parameters that occurred during the experiments i.e. the temperature changing during DAF operations and the variations of raw water qualities. However, errors due to these factors were reduced by increasing the number of replicate runs in the experiments.

During the DAF operation, it was not easy to control the level of liquid and the gas pressure in the air saturator at a steady value over a long period of time. The valves needed to be regulated every 3-5 minutes to maintain a stable condition. Since both the levels of pressure and the liquid height in the saturator may influence the amounts of air dissolved in the saturator, the pressure was controlled to \pm 0.2 barg, while the height of liquid was operated in the range of \pm 3 cm.



Figure 5.1 Flocculation bench with control box and agitator dimensions.



Figure 5.2 Rank Brothers' apparatus: modified rectangular flat cell.



Figure 5.3 Rank Brothers' apparatus: 1 = DC power supply; 2 = light source; 3 = controller; 4 = modified cell immersed in water bath; 5 = VCR system.



Figure 5.4 Malvern Zetamaster: 1 = sample injection point; 2 = quartz cell.



Figure 5.5 Floc strength testing rig: 1 = peristaltic pump connected to side taps; 2 = stirred tank; 3 = regulated speed motor; 4 = Lasentec probe.



Figure 5.6 Agitated tank with torque measuring equipment: 1 = platform scale; 2 = pulley and support; 3 = lever arm connected with string; 4 = bearing.



Figure 5.7 Semicontinuous flotation rig : 1 = air compressor; 2 = tap water tank; 3 = saturator; 4 = flotation column; 5 = VCR system; 6 = motor and gear box; 7 = holding tank; 8 = separating tank; 9 = underflow pipe.



Figure 5.8 Valve and instrument arrangements for the air saturator.

Chapter 6

Results and discussion: Measurements of interfacial forces

6.1 Introduction

This chapter discusses the results obtained from the measurements of the zeta potentials of both bubbles and clay suspensions treated with coagulants or surfactants. Two other interfacial forces, van der Waals and hydrophobic forces, will be investigated using contact angle measurements. The raw data are shown in Appendix C. Free energies obtained in this chapter will be used to explain the results of flocculation and flotation tests in Chapter 7 and Chapter 8, respectively. Moreover, the calculated Hamaker constants and hydrophobic force parameters will be used to explain the flocculation phenomena in Chapter 7 and in a flotation model in Chapter 9.

6.2 Measurements of zeta potentials of bubbles

The values of the zeta potentials of the bubbles in aqueous solutions of 10^{-2} mol/L of sodium sulphate with 5 x 10^{-5} mol/L of hexadecyltrimethylammonium bromide (HTAB) given in Table 6.1 and similar solutions of 10^{-3} mol/L of aluminium sulphate with 10^{-4} mol/L of sodium dodecyl sulphate (SDS) given in Table 6.2 are slightly different from the measurements of earlier workers.

The results in Table 6.1 show an error in the present measurement to be about 10% but that increases to about 30% for the results shown in Table 6.2. This is may be because the pH of a solution is different from Okada and Akagi's work. However, the values are still in the same order of magnitude as those of earlier workers. It is considered that this technique is good enough to measure the zeta potentials of bubbles in further experiments.

Table 6.1 Zeta potentials of bubbles measured in aqueous solutions with 10^{-2} mol/L sodium sulphate, 5 x 10^{-5} HTAB mol/L and 0.5% (v/v) ethanol.

zeta potential (mV)	standard deviation of data	references
+50	10 % of the mean	Collins et.al. [14]
+48*	no data	Okada and Akagi [11]
+56	20 % of the mean	Fukui and Yuu [22]
+45.4	5.2	this work

* read from the article graph

Table 6.2 Zeta potentials of bubbles measured in aqueous solution with 10^{-3} mol/L aluminium sulphate and 10^{-4} mol/L SDS, the pH of a tested solution is 3.7.

zeta potential (mV)	standard deviation of data	references
+5*	no data	Okada and Akagi [11]
+9.6	2.9	this work

* read from the article graph

6.2.1 Effect of cationic surfactants on the electromobilities of bubbles

Figure 6.1 shows the effect of dodecyltrimethylammonium bromide (DTAB) on the electromobilities of the bubbles. At low concentrations of surfactant, it was difficult to generate bubbles due to the low conductivity so in the range of surfactant concentrations between 0 and 3.2×10^{-6} mol/L (0-1 mg/L), 1.7×10^{-5} mol/L (1 mg/L) of NaCl was added. When the DTAB concentrations were higher than 3.2×10^{-6} mol/L, electromobility measurements were performed on the solutions without sodium chloride addition. The average size of the bubbles in the experiments is 27 µm and an error bar shows the standard deviation on each electromobility measurement which gives an average error of approximately 25% from the mean. The mobilities of bubbles decreased with decreasing DTAB concentrations and gave a constant value at a monolayer coverage in the surfactant concentration range of 10^{-6} - 10^{-3} mol/L.



Figure 6.1 Bubble electromobilities in DTAB solutions with distilled water and in the presence of 1 mg/L of NaCl at low concentrations.

Figure 6.2 and Figure 6.3 show the relationship between the electromobilities and the tetradecyltrimethylammonium bromide (TTAB) and (HTAB) concentrations. In both cases, again, the average bubble sizes are 27 μ m and the average error from the mean is 35% approximately.



Figure 6.2 Bubble electromobilities in TTAB solutions with distilled water and in the presence of 1 mg/L of NaCl at low concentrations.

The surfactant monolayer occurred at concentrations between 10^{-8} - 10^{-4} mol/L for TTAB and 10^{-9} - 10^{-5} mol/L for HTAB respectively. The electromobilities of the bubbles decrease as both surfactant concentrations are reduced until the charges change from positive to negative.

In comparison to Kubota and Jameson's measurement [25], the points of zero charge of nitrogen bubbles measured in DTAB, TTAB and HTAB solutions are different. The reason for these results is unclear but it is likely that they are due to bubble size differences during zeta potential measurements and this will be discussed in section 6.2.2. Another contributory factor is that bubble concentrations were different. The surfactant molecules adsorb on bubble surfaces so the number of bubbles introduced into the cell will give different results.



Figure 6.3 Bubble electromobilities in HTAB solutions with distilled water and in the presence of 1 mg/L of NaCl at low concentrations.

Figure 6.4 presents the relationship between bubble electromobility and concentration for three types of surfactant solutions. In comparison between the results of zeta potentials measured in a monolayer coverage (a plateau region), the electromobilities of the bubbles measured in HTAB are slightly higher than those obtained in TTAB and DTAB solutions but the points of the zero charge are different. By using a regression technique, the isoelectric point for bubbles in each surfactant solution was estimated to occur at concentrations of 1.61×10^{-9} mol/L for HTAB, 1.69×10^{-8} mol/L for TTAB and 2.37×10^{-7} mol/L for DTAB, respectively. These values will be used to estimate transfer energies as follows.



Figure 6.4 Bubble electromobilities and the concentrations in three types of cationic surfactant (DTAB, TTAB and HTAB) solutions.

According to Somasundaran and co-workers [69] as described in section 3.6.2, the adsorption of positive counterions at the shear plane is given by:

$$\Gamma_{\delta}^{+} = 2r_{\delta s}C\exp(-W_{\delta s}/k_{B}T)$$
(3.38)

and

$$\ln C_0 = -n_c(\phi'/k_BT) - \ln(\Gamma_{\delta s}^+)_0 - \ln(2r_{\delta s})$$
(3.41)

When the points of zero charge of bubbles measured in surfactant solutions are plotted against the number of carbon atoms in the alkyl chain, n_c , the transfer energy will be obtained from a slope.

Figure 6.5 shows the relationship between the concentrations of n-alkyl-TAB at the point of zero charge and the total number of carbon atoms in the alkyl chain. By

using a linear regression technique, the transfer energy can be obtained as $-1.248k_BT$. This value is slightly higher than a value of $-1.18k_BT$ obtained from Kubota and Jameson's work [25] by using dissolved nitrogen gas. However, both values are smaller than the $-1.39k_BT$ given for the complete transfer of substance from the liquid phase to the non-aqueous phase. It can be concluded that the bubbles were neutralised by cationic surfactants but the bubble surface was not completely covered by surfactant molecules. This result agrees with Lin and Somasundaran's report [102].



Figure 6.5 The concentrations of n-alkyl-TAB at the isoelectric point and the total number of carbon atoms in the alkyl chain.

6.2.2 Effect of bubble sizes on the electromobilities of bubbles

Table 6.3 shows the concentrations at the point of zero charge of bubbles in cationic surfactants compared with some literature values. When the present data are compared with that of Kubota and Jameson [25], the points of zero charge seem to be

different by about three orders of magnitude for all types of surfactant. For DTAB, however, the results show that the points of zero charge are different in one order of magnitude at different pH and average bubble size values when the data are compared with the results of Brandon and co-workers [23]. Their results also showed that the zeta potentials of oxygen and hydrogen bubbles at 10^{-3} mol/L of sodium sulphate in the pH range of 4-10 were increased when the bubble diameters were increased from 30 µm to 200 µm. Moreover, Brandon and co-workers reported the zeta potential of bubbles at pH 2.4 to be positive in the concentration range of 10^{-8} - 10^{-3} mol/L. In comparison Usui and Sasaki [19] who measured the zeta potential of bubbles with a sedimentation technique found that the bubbles in a concentration of HTAB solution of about 3 x 10^{-7} mol/L were still positively charged. Although all of these results in HTAB solution cannot to be compared directly because different measurement techniques were used, it should be noted that bubble size and experimental conditions may have an effect on the value of the charge on the bubble. Surfactant adsorption and ionic strength are also parameters effecting the zeta potential of particles and bubbles.

Table 6.3 The concentrations at the point of zero charge of bubbles in cationic surfactants measured by electrophoresis and sedimentation potential techniques.

Type of cationic	concentration at	Ave. bubble	pН	Techniques	Ref.
surfactant	(p.z.c)* (mol/L)	size (µm)			
DTAB	1×10^{-4}	4	5.6	electrophoresis	25
DTAB	1×10^{-6}	100	6.9	electrophoresis	23
DTAB	2.3×10^{-7}	27	5.6	electrophoresis	this work
TTAB	4×10^{-4}	4	5.6	electrophoresis	25
TTAB	1.7×10^{-8}	27	5.6	electrophoresis	this work
HTAB	1×10 ⁻⁶	4	5.6	electrophoresis	25
HTAB	1.6×10^{-9}	27	5.6	electrophoresis	this work
НТАВ	3×10 ⁻⁷ **	540	-	sedimentation	19

* is the point of zero charge

** read at the lowest value from the report; zeta potential is still positive

At equilibrium, the number of moles on the bubble surface is ΓA_b where Γ is surface excess (mole/cm²) and A_b is the surface area of bubble. For a dilute solution, Gibbs' equation can be written as follows:

$$\Gamma = -\frac{C}{\beta RT} \frac{\mathrm{d}\gamma_L}{\mathrm{d}C}$$
(3.36)

where C is the bulk concentration of surfactant and γ_L is the surface tension. The constant β is given a value of 1 in dilute electrolyte solution and 2 in dilute surfactant solution [63]. For HTAB solution, $d\gamma_L/dC$ can be estimated to be -3.3 x 10⁷ dyne-cm²/mole at a concentration of 5 x 10⁻⁵ mol/L [14]. At the point of zero charge, the surface excess in the absence of electrolyte can be calculated from equation (3.36) giving the values as follows:

from the present data in the presence of electrolyte ($\beta = 1$)

$$\Gamma$$
 = 2.14 x 10⁻¹⁵ moles/cm² for HTAB

$$\Gamma A_b = 4.9 \times 10^{-20} \text{ moles} \qquad (d_p = 27 \,\mu\text{m})$$

from the data of Kubota and Jameson [25] give

$$\Gamma$$
 = 6.66 x 10⁻¹³ moles/cm² for HTAB

$$\Gamma A_b = 3.35 \times 10^{-19} \text{ moles} \qquad (d_p = 4 \,\mu\text{m})$$

In comparison to Kubota and Jameson's tests, the surface excess is different by two orders of magnitude, while the number of moles give a difference about one order of magnitude.

6.3 Zeta potential measurements of clay suspensions

Representative samples of the clays, kaolin and Wyoming bentonite were analysed by the Natural History Museum [97] and have the properties shown in Table 6.4 .

Properties	Kaolin	Wyoming bentonite	
Cation exchange capacity (meq/100g)	12.5	63.1	
Density (g/cm)	2.6	2.8	
Purity (%)	90	93	

Table 6.4 The properties of clays used in the present tests (after Jefferson [97]).

Zeta potentials of both kaolin and Wyoming bentonite suspensions prepared in tap water (see water qualities in Appendix B) were measured during flocculation tests and flotation tests. The zeta potentials of kaolin suspensions treated with HTAB are shown in Figure 6.6. The results show that the particle charges of samples taken in both flocculation and flotation tests are independent of HTAB concentrations in the range of 1×10^{-6} to 2×10^{-5} mol/L and the average value is about -20 mV. The zeta potential of kaolin suspensions then increases with increasing HTAB concentrations and the point of zero charge is at about 1.8×10^{-4} mol/L. This isoelectric point gave a different value compared to Jefferson's report [97] using the same clay materials where the point of zero charge was claimed to be at about 1.1×10^{-5} mol/L of HTAB in kaolin suspensions diluted with distilled water. The reasons for the variance of the isoelectric point is not fully understood but it may be explained that due to ionic strength and pH differences between suspensions prepared from tap water (pH 7.4) and distilled water (pH 5.6). Black and Hannah [31] reported from experiments that kaolin suspensions treated with 5 ppm of alum gave the point of zero charge at pH 5.6 but the electromobility was negative at pHs above 6.0.

For Wyoming bentonite suspensions treated with HTAB, the zeta potentials are shown in Figure 6.7. The charges on particle samples obtained from both flocculation

and flotation tests are independent of HTAB concentrations in the range of 1×10^{-6} to 1×10^{-5} mol/L and the average value is about -23 mV. The zeta potentials on Wyoming bentonite particles in the solution increased greatly with increasing HTAB concentrations and reached the point of zero charge at about 3×10^{-5} mol/L. This isoelectric point may be compared with the value given in Jefferson's report [97] where the point of zero charge was claimed to be at about 1.5×10^{-5} mol/L of HTAB for Wyoming bentonite suspensions diluted with distilled water.



Figure 6.6 The zeta potentials of kaolin particles at a concentration of 50 mg/L in HTAB solutions.

In comparison to similar kaolin suspensions, Wyoming bentonite suspensions dosed with HTAB exhibited an isoelectric point one order of magnitude smaller. The explanation is unclear but it has been suggested that the effect of pH on kaolin electromobility was more sensitive than on montmorillonite mobility. Black and Hannah [31] measured the zeta potentials of montmorillonite and kaolin suspensions treated with 5 mg/L of alum and they found negative charges in the range of pH 3.5-10 for montmorillonite while kaolin exhibited positive charges in the range of pH 5-5.5. Another contributory factor is that kaolin suspensions dosed with HTAB do not

form flocs, therefore, only surfactant molecules adsorbed on the kaolin surfaces are effective in reducing particle charges. On the other hand, with the Wyoming bentonite flocs are formed, which adsorb greater concentrations of surfactant on the particle surfaces and by entrapment between the particles in the flocs.



Figure 6.7 The zeta potentials of Wyoming bentonite particles at a concentration of 50 mg/L in HTAB solutions.

The observations showed that Wyoming bentonite suspensions were able to produce flocs by addition of HTAB while the kaolin suspensions did not form such aggregates. One flocculation mechanism is believed to be that ions in the suspensions such as Ca^{2+} and Na^+ are a major cause in promoting destabilisation. This hypothesis was supported by Lagaly [103] who suggested that montmorillonite suspensions responded to critical coagulation concentrations, a minimum ion concentration promoting coagulation, at lower values than those in comparable kaolin suspensions in the pH range of 4-10. He also claimed that the presence of 10^{-3} mol/L calcium ions in natural water increased the aggregation rate of Wyoming bentonite treated with cationic polymer by compressing the diffuse ions around the particles and the flocculation was propagated by bridging. At concentrations lower than the critical

concentration, the distance between the particles is too large to be spanned by macromolecules so flocs cannot be formed.

Figure 6.8 and Figure 6.9 present the zeta potentials of kaolin suspensions at concentrations of 50 mg/L and 100 mg/L, respectively, when treated with three coagulants, alum, ferric chloride and polyaluminium chloride (PAC). The results show that the particle charges on both suspensions dosed with each coagulant increase with increasing concentrations. The points of zero charge are at about 50 mg/L for both alum and ferric chloride treatment and at around 10 mg/L for PAC. These isoelectric points have different values compared to those shown in Jefferson's report [97] where the points of zero charge were claimed to be at 4 mg/L for alum and about of 1 mg/L for ferric chloride dosed in kaolin suspensions diluted with distilled water. Again, this may that due to ionic strength and pH differences between suspensions prepared from tap water and distilled water. Black and Chen [32] supported that explanation from their zeta potential measurements using three river sediment suspensions diluted with tap water and coagulated with aluminium sulphate. Their results showed that the zeta potentials of all suspensions dosed with alum up to 10 mg/L were negative and the positive charges were exhibited only in the pH range of 4.5-6.5 when alum addition was 50 mg/L.



Figure 6.8 The zeta potentials of 50 mg/L kaolin suspensions treated with coagulants.



Figure 6.9 The zeta potentials of 100 mg/L kaolin suspensions treated with coagulants.



Figure 6.10 The zeta potentials of 50 mg/L Wyoming bentonite suspensions treated with coagulants.

For Wyoming bentonite suspensions dosed with the three coagulants, Figure 6.10 and Figure 6.11 show the zeta potentials of particles at concentrations of 50 mg/L and 100 mg/L, respectively. The zeta potentials of both suspensions treated with each

coagulant increase with increasing concentrations. The points of zero charge are at about 100-130 mg/L for both alum and ferric chloride additions and in the range of 30-40 mg/L for PAC. In comparison Jefferson's measurements [97], which were performed with the same clay materials, claimed the isoelectric points to be 40 mg/L for both alum and ferric chloride addition. Again, this may that due to ionic strength and pH differences between suspensions prepared from tap water and distilled water.

The zeta potential measurements will be used to explain the results of flocculation tests, flotation tests and an electrostatic interaction between particles and bubbles in flotation models.



Figure 6.11 The zeta potentials of 100 mg/L Wyoming bentonite suspensions treated with coagulants.

6.4 Measurements of contact angle

6.4.1 Kaolin surfaces

Kaolin surfaces prepared as described in Chapter 5 were used in the measurements of contact angles with four liquids; water, glycerol, diiodomethane (DIM) and 1-bromonapthalene (BNL). The results are shown in Figure 6.12 for kaolin-HTAB

surfaces and in Figure 6.13 to Figure 6.15 for kaolin-coagulant surfaces. The contact angles of the kaolin-HTAB surfaces increased slightly with increasing HTAB concentrations and it seems that a surface saturation concentration was not obtained in the concentration range of 0 to 5 x 10^{-5} mol/L. However, Pashley and Israelachvili [104] and Eriksson and co-workers [105] claimed a monolayer coverage of HTAB on mica from about 3 x 10^{-5} mol/L to 5 x 10^{-4} mol/L.



Figure 6.12 Contact angles of kaolin surfaces prepared from flocs coagulated in HTAB solutions (DIM = diiodomethane and BNL = 1-bromonapthalene).

Two hydrophilic liquids, water and glycerol, exhibited contact angles on kaolin surfaces higher than those obtained with two hydrophobic liquids, DIM and BNL. These indicate that a hydrophobic force is increased with increasing HTAB concentrations, a result which will be confirmed in section 6.5 by comparing the free energies. Yoon and Ravishankar [106, 107] also showed that the high contact angles measured using water in the range up to 90 degrees representing the high hydrophobic forces.


Figure 6.13 Contact angles of kaolin surfaces prepared from flocs in various concentrations of alum solutions.



Figure 6.14 Contact angles of kaolin surfaces prepared from flocs in various concentrations of ferric chloride solutions.

The understanding of the hydrophobic mechanism may be unclear but hydrophobic interactions occur normally in a system where an organic compound is present in aqueous solution. A simple concept may be used to explain effects in a binary system

in which organic molecules of phase (1) are present in an aqueous phase (3). If the coalescence of the organic molecules occurs spontaneously, the molecules are hydrophobic. On the other hand, if the reverse process obtains spontaneously, the organic molecules are hydrophilic [75]. For example, carbon tetrachloride is a hydrophobic compound with molecules attracting each other in water forming an immiscible layer while polyethylene oxide is hydrophilic with the molecules repelling each other in water and becoming dispersed. In a flotation process, when bubbles are introduced into a flotation cell containing hydrophobic particles, one possible mechanism in attaching bubbles to particle surfaces is caused by hydrophobic forces. The indicative parameter for the flotation is the free energy of materials (1) and (2) in medium (3), ΔG_{132}^T , which will be discussed later.



Figure 6.15 Contact angles of kaolin surfaces prepared from flocs in various concentrations of PAC solutions.

Contact angle measurements of the kaolin-coagulant surfaces with apolar and polar liquids in Figure 6.13 to Figure 6.15 are all reasonably constant within 5-10 degrees. This suggests that both hydrophobic and hydrophilic forces become independent of the concentrations of coagulants in the range of 40-60 mg/L for alum and ferric chloride, and in the range of 10-20 mg/L for PAC. The hydrophilic forces in this case

can be named as hydration forces created from adsorbed hydrated cations or metal hydroxide [108].

6.4.2 Wyoming bentonite surfaces

Contact angles were measured on Wyoming bentonite surfaces using the same four liquids and the results are shown in Figure 6.16 for Wyoming bentonite-HTAB surfaces and Figure 6.17-6.19 for Wyoming bentonite-coagulant surfaces. Again the contact angles on the Wyoming bentonite-HTAB surfaces increased slightly with increasing HTAB concentrations and became constant at HTAB concentration about 2×10^{-5} mol/L. A saturation concentration of Wyoming bentonite-HTAB surfaces has also been reported in this range of concentration [97].



Figure 6.16 Contact angles of Wyoming bentonite surfaces prepared from flocs in HTAB solutions.

The hydrophobicity of Wyoming bentonite surfaces was increased with the addition of HTAB. The water contact angles were increased from about 20 degree to 65 degree. This contact angle value agreed well with Pashley and co-workers' measurements [104, 109, 110] showing an advancing contact angle of 65 degree on a mica surface treated with 10⁻⁴ mol/L of HTAB. Eriksson and co-workers [105] also

claimed a maximum contact angle of about 70 degree for 5×10^{-5} mol/L of HTAB on mica. Their results also showed a decrease of contact angle when HTAB concentrations were increased above 5×10^{-5} mol/L and a critical micelle concentration (CMC) was obtained when HTAB concentrations increased up to 1×10^{-3} mol/L.



Figure 6.17 Contact angles of Wyoming bentonite surfaces prepared from flocs in various concentrations of alum solutions.



Figure 6.18 Contact angles of Wyoming bentonite surfaces prepared from flocs in various concentrations of ferric chloride solutions.



Figure 6.19 Contact angles of Wyoming bentonite surfaces prepared from flocs in various concentrations of PAC solutions.

Contact angle measurements of the Wyoming bentonite-coagulant surfaces with apolar and polar liquids shown in Figure 6.17 to Figure 6.19 are all reasonably constant. Again, this suggests that both hydrophobic and hydrophilic forces are independent of the concentrations of coagulants in the range of 40-60 mg/L for alum and ferric chloride, and in the range of 10-20 mg/L for PAC.

The contact angle data were used to determine surface energies and free energies as described below.

6.5 Surface energy and free energy

According to van Oss [111-114], the Young-Dupre equation (6.1) can be rewritten as:

$$-\Delta G_{sL} = \gamma_L (1 + \cos\theta) \tag{6.1}$$

$$-\Delta G_{SL}^{LW} - \Delta G_{SL}^{AB} = \gamma_L (1 + \cos\theta)$$
(6.2)

where ΔG_{SL} is the free energy of the solid-liquid interface, ΔG_{SL}^{LW} is the apolar free energy of the solid-liquid interface, ΔG_{SL}^{AB} is the polar free energy of the solid-liquid interface, γ_L is the liquid surface tension and θ is the contact angle. Equation (6.2) can be presented in the Young-Good-Girifalo-Fowkes equation as:

$$\gamma_L(1+\cos\theta) = 2(\sqrt{\gamma_S^{LW}\gamma_L^{W}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+})$$
(6.3)

where γ_{S}^{LW} is the apolar surface energy of the solid, γ_{L}^{LW} is the apolar surface tension of the liquid, γ_{S}^{+} and γ_{S}^{-} are the electron acceptor and electron donor surface energies of the solid, and γ_{L}^{+} and γ_{L}^{-} are the electron acceptor and electron donor surface tensions of the liquid. When contact angles are measured using an apolar liquid such as diiodomethane, DIM, in which $\gamma_{L}^{LW} = \gamma_{L}$, equation (6.3) becomes:

$$1 + \cos\theta = 2\sqrt{\gamma_s^{LW} / \gamma_L}$$
 (6.4)

The surface energies of the solid were determined using contact angle measurements with three liquids at least, 1 apolar and 2 polar liquids. The apolar surface energy of a solid may be calculated from equation (6.4) using a contact angle measured with an apolar liquid of a known surface tension. Substituting contact angles measured with 2 polar liquids in equation (6.3), the polar surface energies of solid, γ_s^+ and γ_s^- , were obtained (see Appendix E4 for a detail calculation).

Van Oss and co-workers present the free energies relating to the surface energies given in equations (3.49) and (3.50).

$$\Delta G_{131}^{LW} = -2(\sqrt{\gamma_1}^{LW} - \sqrt{\gamma_3}^{LW})^2 \qquad (3.49)$$

$$\Delta G_{132}^{LW} = -2(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}})(\sqrt{\gamma_2^{LW}} - \sqrt{\gamma_3^{LW}}) \quad (3.50)$$

In equation (3.50), if material (2) is an air bubble $(\gamma_2^{LW} \le \gamma_3^{LW})$, the equation can be rewritten as:

$$\Delta G_{132}^{LW} = 2(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}}) \sqrt{\gamma_3^{LW}}$$
(6.5)

van Oss also defined the polar free energy as:

$$\Delta G_{ii}^{AB} \equiv -4\sqrt{\gamma_i^+ \gamma_i^-} \tag{6.6}$$

By using the Dupre equation, both free energies, ΔG_{131}^{AB} and ΔG_{132}^{AB} , can be given as:

$$\Delta G_{131}^{AB} = -4(\sqrt{\gamma_{1}^{+}} - \sqrt{\gamma_{3}^{+}})(\sqrt{\gamma_{1}^{-}} - \sqrt{\gamma_{3}^{-}})$$
(6.7)

$$\Delta G_{132}^{AB} = 2 \left[\sqrt{\gamma_{3}^{+}} (\sqrt{\gamma_{1}^{-}} + \sqrt{\gamma_{2}^{-}} - \sqrt{\gamma_{3}^{-}}) + \sqrt{\gamma_{3}^{-}} (\sqrt{\gamma_{1}^{+}} + \sqrt{\gamma_{2}^{+}} - \sqrt{\gamma_{3}^{+}}) - \sqrt{\gamma_{1}^{+}\gamma_{2}^{-}} - \sqrt{\gamma_{1}^{-}\gamma_{2}^{+}} \right]$$

$$(6.8)$$

Again, when material (2) is an air bubble ($\gamma_2^- = \gamma_2^+ \approx 0$), equation (6.8) is reduced to

$$\Delta G_{132}^{AB} = 2 \left[\sqrt{\gamma_{3}^{+}} (\sqrt{\gamma_{1}^{-}} - \sqrt{\gamma_{3}^{-}}) + \sqrt{\gamma_{3}^{-}} (\sqrt{\gamma_{1}^{+}} - \sqrt{\gamma_{3}^{+}}) \right]$$
(6.9)

The surface energy results obtained from contact angle data are presented in Tables 6.5-6.8. Apolar surface energies (LW) in HTAB for both kaolin and Wyoming bentonite have nearly the same value as shown in Figure 6.20.

Both apolar curves decrease slightly from 43 mJ/m² to 31 mJ/m² approximately when HTAB concentrations are increased. This suggests that an attractive force due to van der Waals interaction is reduced and suspensions will be stabilised if HTAB concentrations are increased further. On the other hand, polar surface energies (AB) for an electron donor, $\gamma_{\bar{s}}$, represent a repulsive force due to polar particle interaction. The polar surface energies (AB) for an electron donor are decreased with increasing HTAB concentrations and Wyoming bentonite resists the reduction of repulsion better

than kaolin dosed with HTAB. This suggests that Wyoming bentonite suspensions in HTAB can form flocs easier than Kaolin in HTAB.



Figure 6.20 Surface energy of kaolin and Wyoming bentonite in various concentrations of HTAB solutions: LW = apolar surface energy, KL = kaolin, WB = Wyoming bentonite, and SE+ and SE- = polar surface energy for an electron acceptor and donor.

Table 6.5 Total surface energy of clay surfaces treated with HTAB solutions (see detail calculations in Appendix E4).

Туре	HTAB	γ_{S}^{LW}	γ_{S}^{+}	$\gamma \overline{s}$	γ_{S}^{AB}	γ_{S}^{TOT}
	conc.	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)
	(mol/L)	()	()			
Kaolin	0	43.06	1.68	35.64	15.48	58.54
	1.00E-06	38.92	0.17	31.52	4.70	44.62
	5.00E-06	36.46	0.22	29.72	5.12	41.58
	1.00E-05	34.76	0.20	28.21	4.81	39.57
	2.00E-05	33.42	0.28	26.29	5.47	38.89
	3.00E-05	33.30	0.37	24.23	5.97	39.27
	5.00E-05	31.61	0.88	20.02	8.41	40.02
WB	0	43.53	2.07	40.22	18.26	61.79
	1.00E-06	39.37	0.53	37.41	8.92	48.29
	5.00E-06	37.17	0.44	23.05	6.35	43.52
	1.00E-05	36.32	0.54	22.23	6.96	43.28
	2.00E-05	35.33	0.95	16.06	7.81	43.14
	3.00E-05	35.24	0.67	14.93	6.33	41.57
	5.00E-05	34.46	0.73	15.05	6.62	41.08

Туре	Alum	γ_{S}^{LW}	γ_{s}^{+}	Ϋ́s	γ_{S}^{AB}	γ_{S}^{TOT}
	conc. (mg/L)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)
Kaolin	40	41.60	1.18	40.22	13.78	55.39
	50	41.32	1.53	38.20	15.28	56.60
	60	40.78	1.60	40.12	16.05	56.83
	(40)*	40.09	0.17	26.92	4.25	44.31
WB	40	42.16	0.34	50.55	8.31	50.47
	50	42.17	0.86	42.56	12.10	54.81
	60	43.10	0.66	43.79	10.78	53.88
	(40)*	40.06	1.61	26.39	4.55	44.64

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Table 6.6	Total	surface	energy	of clay	surfaces	dosed	with	alum	solution.

* Suspensions treated with indicated coagulant concentration and 1×10^{-5} of HTAB.

Table 6.7 Total surface energy of clay surfaces dosed with ferric chloride solution.

Туре	FeCl ₃	γ_{S}^{LW}	γ_s^+	$\gamma \bar{s}$	γ_{S}^{AB}	γ_{s}^{TOT}
	conc. (mg/L)	(mJ/m^2)	(mJ/m ²)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)
Kaolin	40	41.15	0.54	45.56	9.95	51.10
	50	41.84	0.87	45.14	12.51	54.35
	60	42.62	0.94	44.56	12.94	55.56
	(40)*	40.02	0.42	27.33	6.78	46.80
WB	40	42.70	1.10	44.30	13.96	56.66
	50	43.20	1.16	40.13	13.63	56.16
	60	42.12	0.59	45.27	10.37	52.49
	(40)*	41.21	0.24	26.90	5.10	45.02

* Suspensions treated with indicated coagulant concentration and 1×10^{-5} of HTAB.

Table 6.8	Total surface	energy of clay	surfaces	dosed	with	PAC	solution.
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Туре	PAC conc. (ma/L)	γ_{S}^{LW}	$\gamma_{S_{2}}^{+}$	γ _s	γS^{AB}_{S}	γ_{S}^{TOT}
	(mg/L)	(mJ/m ²)	(mJ/m²)	(mJ/m^2)	(mJ/m ²)	(mJ/m ²)
Kaolin	10	40.62	0.24	36.04	5.85	46.47
	15	41.82	0.32	38.09	6.94	48.75
	20	42.67	0.34	44.63	7.75	50.42
	(10)*	39.75	0.73	27.35	8.94	48.69
WB	10	42.92	1.19	44.44	14.53	57.69
-	15	42.50	0.49	49.89	9.91	52.41
	20	42.40	0.38	48.85	8.67	51.07
	(10)*	40.78	0.24	26.97	5.05	44.53

* Suspensions treated with indicated coagulant concentration and 1×10^{-5} of HTAB.

In contrast, apolar surface energies (LW) of both clays in solutions of each of the three coagulants are largely independent of coagulant types and concentrations. The results in Tables 6.6-6.8 give the average energy (LW) to be about 41 mJ/m^2 .

The total surface energies, γ_{S}^{TOT} , in Table 6.5 also decrease when HTAB concentrations are increased while the energies of clay-coagulant surfaces in Tables 6.6 to 6.8 are constant. For the surfaces treated with both HTAB and coagulants, all results showed that the total energies decreased in accordance with a decrease in polar surface energy (AB). The γ_{S}^{TOT} of clay-HTAB surfaces given in Table 6.5 agreed with Pashley and Israelachvili [104] who claimed that the solid-vapour surface energy was 42 mN/m² on a mica surface treated with 10⁻⁴ mol/L of HTAB.

The results are shown as free energies in Figure 6.21 and Table 6.9 where ΔG_{131}^T , the free energy of material (1) in medium (3) excluding electrostatic force, decreases from positive values to negative values when the HTAB solution concentration is increased. This result agrees well with those of the flocculation experiments described in Chapter 7 showing that Wyoming bentonite suspensions treated with HTAB produce good flocculation in the concentration range of 5 x 10⁻⁶ to 5 x 10⁻⁵ mol/L while kaolin suspensions only give small flocs at high concentrations of HTAB.

 ΔG_{132}^T represents the interaction between the three phases, 1 = particle, 2 = air and 3 = water excluding electrostatic forces. The values of ΔG_{132}^T obtained from Tables 6.9-6.12 all have negative values. These suggest that flotation may occur in all conditions tested and the addition of HTAB can produce higher removal efficiencies than in a system without HTAB. These results are supported by those of flotation tests as described in Chapter 8.



Figure 6.21 Free energies of kaolin and Wyoming bentonite in HTAB solutions: G131 = ΔG_{131}^T , G132 = ΔG_{132}^T , KL = kaolin and WB = Wyoming bentonite.

Table 6.9 Free energies of clay surfaces treated with HTAB solutions (see detail calculations in Appendix E4).

Туре	HTAB	ΔG_{131}^{LW}	ΔG_{131}^{AB}	ΔG_{131}^T	ΔG_{132}^{AB}	ΔG_{132}^{LW}	ΔG_{132}^T
	conc.	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)
	(mol/L)				· · ·		
Kaolin	0	-7.17	13.82	6.65	-28.61	17.68	-10.93
_	1.00E-06	-4.93	10.46	5.53	-41.07	14.66	-26.41
	5.00E-06	-3.75	7.36	3.61	-42.19	12.51	-29.68
	1.00E-05	-3.01	4.81	.037	-43.78	11.46	-32.32
	2.00E-05	-2.47	1.40	-1.07	-44.83	10.37	-34.46
	3.00E-05	-2.43	-2.26	-4.69	-46.16	10.28	-35.88
	5.00E-05	-1.82	-9.45	-11.27	-47.31	8.88	-38.43
WB	0	-7.44	18.66	11.22	-23.41	18.01	-5.40
	1.00E-06	-5.16	18.43	13.50	-32.87	14.99	-17.88
	5.00E-06	-4.08	-4.36	-8.44	-46.83	13.33	-33.50
	1.00E-05	-3.69	-5.77	-9.46	-46.93	12.68	-34.25
	2.00E-05	-3.25	-16.98	-20.23	-51.68	11.90	-39.78
	3.00E-05	-3.21	-20.07	-23.28	-54.71	11.83	-42.88
	5.00E-05	-2.89	-19.65	-22.54	-54.21	11.22	-42.99

Hydrophobic interactions are represented by the polar free energy (AB) term and Table 6.9 shows the decrease of the polar free energies, in the other word an increase of the hydrophobic forces, with increasing HTAB concentrations. Tables 6.10-6.12 also present both apolar and polar free energies of clay-coagulant surfaces. Apolar free energies, ΔG_{131}^{LW} and ΔG_{132}^{LW} , seem to be constant when the concentrations of coagulants are increased. These results show little effect of a 1 x 10⁻⁵ mol/L of HTAB addition on apolar free energy. This may suggest that polar interaction becomes dominant when coagulants are dosed.

Туре	Alum	ΔG_{131}^{LW}	ΔG_{131}^{AB}	ΔG_{131}^T	ΔG_{132}^{AB}	ΔG_{132}^{LW}	ΔG_{132}^T
	conc.	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)
	(mg/L)	, ,	. ,	Ň,			
Kaolin	40	-6.34	20.49	14.15	-26.97	16.63	-10.34
	50	-6.19	17.25	11.06	-27.09	16.43	-10.66
	60	-5.89	19.44	13.55	-25.23	16.03	-9.20
	(40)*	-5.53	2.58	-2.95	-45.46	15.53	-29.93
WB	40	-6.65	36.80	30.15	-24.29	17.03	-7.26
	50	-6.66	24.31	17.65	-26.74	17.04	-9.70
	60	-7.19	26.56	19.37	-26.94	17.71	-9.23
	(40)*	-5.51	1.61	-3.90	-45.64	15.50	-30.14

Table 6.10 Free energies of clay surfaces treated with alum solutions.

* Suspensions dosed with indicated coagulant concentration and 1×10^{-5} of HTAB.

Туре	FeCl ₃ conc. (mg/L)	$\frac{\Delta G_{131}^{LW}}{(\text{mJ/m}^2)}$	ΔG_{131}^{AB} (mJ/m ²)	$\frac{\Delta G_{131}^T}{(\text{mJ/m}^2)}$	$\begin{array}{c} \Delta G_{132}^{AB} \\ (\text{mJ/m}^2) \end{array}$	$\frac{\Delta G_{132}^{LW}}{(\text{mJ/m}^2)}$	$\frac{\Delta G_{132}^T}{(\text{mJ/m}^2)}$
Kaolin	40	-6.10	29.33	23.23	-26.38	16.30	-10.08
	50	-6.47	27.49	21.02	-24.74	16.80	-7.94

19.62

-2.34

18.75

13.18

22.10

-3.63

-24.79

-42.68

-24.19

-27.16

-26.26

-44.65

-7.43

-27.21

-6.77

-9.38

-9.26

-28.30

17.36

15.47

17.42

17.78

17.00

16.35

Table 6.11 Free energies of clay surfaces treated with ferric chloride solutions.

26.53

3.15

25.71

20.43

28.73

2.50

60

(40)*

40

50

60

(40)*

WB

-6.91

-5.49

-6.96

-7.25

-6.63

-6.13

* Suspensions dosed with indicated coagulant concentration and 1×10^{-5} of HTAB.

Туре	PAC	ΔG_{131}^{LW}	ΔG_{131}^{AB}	ΔG_{131}^T	ΔG_{132}^{AB}	ΔG_{132}^{LW}	ΔG_{132}^T
	conc.	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)	(mJ/m^2)
	(mg/L)	``´`		Ì Ì	``´´	. ,	· · ·
Kaolin	10	-5.81	17.40	11.59	-36.45	15.92	-20.53
	15	-6.46	20.15	13.69	-33.99	16.78	-17.21
	20	-6.94	29.15	22.21	-28.67	17.40	-11.27
	(10)*	-5.35	3.02	-2.33	-40.53	15.27	-25.26
WB	10	-7.09	25.61	18.52	-23.67	17.58	-6.09
	15	-6.85	35.02	28.17	-23.58	17.28	-6.30
	20	-6.79	34.36	27.57	-25.15	17.21	-7.94
	(10)*	-5.90	2.62	-3.28	-44.64	16.03	-28.61

Table 6.12 Free energies of clay surfaces treated with PAC solutions.

* Suspensions dosed with indicated coagulant concentration and 1×10^{-5} of HTAB.

The free energies of clay-coagulant surfaces, ΔG_{131}^T , have positive values as shown in Tables 6.10-6.12 so it is believed that flocculation of the clay suspensions treated with each coagulant may not occur. In contrast, the flocs of similar clay suspensions were observed in flocculation tests. This result will be explaned using non-DLVO theory in Chapter 7.

When HTAB solution is added as well as coagulant, both kaolin-coagulant surfaces and Wyoming bentonite-coagulant surfaces show negative energies. These results suggest that all suspensions treated with HTAB can produce flocs.

6.6 Hamaker constant

Hamaker constants, A_{131} and A_{132} , may be calculated by substituting A_{11} , A_{22} , and A_{33} into equations (3.43) and (3.44).

$$A_{131} = (\sqrt{A_{11}} - \sqrt{A_{33}})^2$$
 (3.43)

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}})$$
(3.44)

When material (1) is a particle, (2) is an air bubble and (3) is water, the Hamaker constant of the air bubble is very much less than the Hamaker constant of water (A_{22} , $<< A_{33}$) so equation (3.44) can be simplified to

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(-\sqrt{A_{33}})$$
 (6.10)

Hunter [76] and Israelachvili [115] reported the Hamaker constant of water (A_{33}) to be 3.7 x 10⁻²⁰ J. This value was supported by Yoon and Mao [74] and Parsegian and Weiss [116] who reported A_{33} values of 4.38 x 10⁻²⁰ J and 4.0 x 10⁻²⁰ J, respectively.

For A_{11} estimation, Fowkes [117] has shown that it can be obtained from the apolar surface energy of solid, γ_S^{LW} , given by:

$$A_{11} = 6\pi r_{11}^2 \gamma_S^{LW}$$
(6.11)

where r_{11}^2 is the interatomic distance in the particle and the value of $6\pi r_{11}^2$ is usually assumed to be 1.44 x 10⁻¹⁸ m² [74]. This value was supported by van Oss [75] who noted that the value of $6\pi r_{11}^2$ was 1.86 x 10⁻¹⁸ m².

Table 6.13 shows the Hamaker constants obtained from contact angle measurements; note that all values are in the range of 10^{-21} - 10^{-20} J. This agreed with Gregory [108] who claimed that the Hamaker constants for aqueous dispersions were in the range of 3 x 10^{-21} to 1 x 10^{-20} J. The A_{131} presents an attractive force while A_{132} is a repulsive force. In HTAB solutions, both the attractive force (A_{131}) and the repulsive force (A_{132}) decreased with increasing HTAB concentrations.

Туре	Chemical	Hamaker constant (x 10 ²¹ J)		
	concentration	A ₁₃₁	A ₁₃₂	
Kaolin	0	8.21	-17.4	
Kaolin in HTAB	1.00E-06 mol/L	5.87	-14.7	
	5.00E-06 mol/L	4.62	-13.1	
	1.00E-05 mol/L	3.83	-11.9	
	2.00E-05 mol/L	3.23	-10.9	
	3.00E-05 mol/L	3.18	-10.9	
	5.00E-05 mol/L	2.50	-9.62	
Kaolin in alum	40 mg/L	7.34	-16.5	
	50 mg/L	7.18	-16.3	
	60 mg/L	6.88	-16.0	
Kaolin in FeCl ₃	40 mg/L	7.09	-16.2	
	50 mg/L	7.48	-16.6	
	60 mg/L	7.94	-17.1	
Kaolin in PAC	10 mg/L	6.79	-15.9	
	15 mg/L	7.47	-16.6	
	20 mg/L	7.97	-17.2	
WB	0	8.48	-17.7	
WB in HTAB	1.00E-06 mol/L	6.11	-15.0	
	5.00E-06 mol/L	4.97	-13.6	
	1.00E-05 mol/L	4.55	-13.0	
	2.00E-05 mol/L	4.08	-12.3	
	3.00E-05 mol/L	4.04	-12.2	
	5.00E-05 mol/L	3.69	-11.7	
WB in alum	40 mg/L	7.67	-16.8	
	50 mg/L	7.67	-16.8	
	60 mg/L	8.22	-17.4	
WB in FeCl ₃	40 mg/L	7.98	-17.2	
	50 mg/L	8.28	-17.5	
	60 mg/L	7.64	-16.8	
WB in PAC	10 mg/L	8.11	-17.3	
	15 mg/L	7.87	-17.1	
	20 mg/L	7.81	-17.0	
Kaolin in HTAB* and alum	alum 40 mg/L	6.31	-15.3	
Kaolin in HTAB* and FeCl ₃	FeCl ₃ 40 mg/L	6.50	-15.5	
Kaolin in HTAB* and PAC	PAC 10 mg/L	6.46	-15.5	
WB in HTAB* and alum	alum 40 mg/L	6.88	-16.0	
WB in HTAB* and FeCl ₃	FeCl ₃ 40 mg/L	6.48	-15.5	
WB in HTAB* and PAC	PAC 10 mg/L	7.12	-16.2	

 Table 6.13 Hamaker constants of clay-chemical surfaces (see detail calculations in Appendix E4).

* HTAB concentration is 1×10^{-5} mol/L.

Yoon and co-workers [118-120] also found a decrease in A_{131} value with increasing contact angles in their measurements of contact angle on silica and silanated silica plates using nanopure water. From flotation tests, Yoon and Mao [74] also claimed an decrease in absolute values of A_{132} for fused silica suspensions in trimethylchlorosiliane (TMCS) solutions at a range of concentrations. This agreed with the results obtained for clay-HTAB surfaces as shown in Table 6.13.

When coagulants are used, both A_{131} and A_{132} are found to be independent of coagulant types over the range of concentrations tested. However, values of A_{131} and A_{132} for clay surfaces dosed with coagulants decreased slightly when these values were compared to the Hamaker constants of clay surfaces without additions.

6.7 Summary

Interfacial forces are an important factor in attachment mechanisms in flotation. Both van der Waals and hydrophobic parameters can be obtained from contact angle measurements. The free energies showed that flocculation and flotation were possible when Wyoming bentonite was treated with HTAB. For kaolin suspensions, only high concentrations of HTAB solutions, above 2×10^{-5} mol/L, were predicted to give flocculation but flotation actually occurred in both cases with and without chemical additions.

Chapter 7

Results and discussion: Flocculation tests

7.1 Introduction

This chapter discusses the results obtained from the flocculation tests on clay suspensions treated with chemicals. The flocculation data obtained from the jar test apparatus are given in Appendix C and the optimal results will be used for the chemical treatment in the flotation tests. Flocculation modelling using the extended-DLVO theory will be described for both kaolin and Wyoming bentonite suspensions. Finally, floc strength is investigated using size distribution measurements of breakage flocs and the result will be used for a flotation model described in Chapter 9.

7.2 Coagulation and flocculation tests

7.2.1 Kaolin suspensions

Removal efficiencies for 50 and 100 mg/L concentrations of kaolin suspensions treated with three coagulants, alum, ferric chloride and polyaluminuim chloride (PAC), are shown in Figures 7.1 to 7.3, respectively. The initial pH of the suspensions was about 7.4 and the pH values of each final solution fell as coagulant concentration was increased, as is shown in Figures 7.4 and 7.5.

The results show that at low coagulant concentrations, flocculation efficiencies for the 50 mg/L kaolin suspension have lower values than those for the 100 mg/L concentration. Black and Chen [33] also found this result in flocculation experiments with kaolin suspensions treated with alum, which showed a decrease in residual turbidity with increasing initial suspension concentration. Obviously, the rate of particle collision in a coagulation process is higher at greater clay suspension

concentrations. In other words, high suspension concentrations when treated with coagulants formed flocs easier than low suspension concentrations because of the reduction in interparticle distances.



Figure 7.1 Flocculation tests of 50 mg/L and 100 mg/L kaolin suspensions with alum solution (the efficiency is defined as a ratio of residual turbidity and untreated suspension turbidity).



Figure 7.2 Flocculation tests of 50 mg/L and 100 mg/L kaolin suspensions with ferric chloride solution.



Figure 7.3 Flocculation tests of 50 mg/L and 100 mg/L kaolin suspensions with PAC solution.

In Figure 7.1 both curves reach a plateau region at a concentration of about 30 mg/L alum. It seems that the optimal alum concentrations are in the range of 30-60 mg/L. For ferric chloride additions, shown in Figure 7.2, the optimal concentrations are in the range of 20-50 mg/L while for PAC Figure 7.3 shows the most effective treatment in the concentration range of 5-40 mg/L.

PAC gave the highest flocculation efficiencies and this result was supported by the work of Dempsey and co-workers [36] who cited the greater charge neutralisation capacity of PAC relative to alum. Polymeric aluminium species are cationic polyelectrolytes or positively charged colloids. The nature of the aluminium species in PAC is not fully understood but it has been reported as variously, monomer, dimer, an Al_{13} polymer and several higher polymer forms [121].

Ferric chloride in the concentration range of 5-20 mg/L gave slightly higher removal efficiencies than alum. Clearly, the number of Fe(III) ions in the clay suspension was higher than Al(III) ions due to a molecular weight difference. This result was in agreement with Johnson and Amirtharajah [40] who showed that Fe(III) could be more effective than alum in kaolin suspensions.



Figure 7.4 pH of 50 mg/L kaolin suspensions with various coagulants.



Figure 7.5 pH of 100 mg/L kaolin suspensions with various coagulants.

When ferric chloride concentrations were increased to values higher than 100 mg/L, the removal efficiencies decreased because restabilisation was found in this region. From the stability diagrams of alum and ferric chloride shown in Figures 2.3 and 2.4, the restabilisation zone for alum coagulation was narrow when compared to that for ferric chloride. Thus, the removal efficiency of suspensions treated with alum seems to be constant. These results agreed with Stumm and O'Melia's work [38] showing that restabilisation did not occur in the alum concentration range of 100-300 mg/L at pH higher than 4. Stumm and O'Melia also showed that the adsorption of hydrolysed metal ions on the surface of the particles was responsible for the destabilisation and restabilisation depending on the stoichiometry between the coagulant and the colloid in the adsorption-destabilisation area.

Figure 2.3 shows that the alum-addition range of 30-60 mg/L in a neutral pH is in a sweep flocculation zone in which precipitated aluminium hydroxide, $Al(OH)_{3(S)}$, is dominant in the destabilisation process. It is believed that the weakly positive charged $Al(OH)_{3(S)}$ reacts directly with the negative charges on the clay surfaces. According to Amirtharajah and Tambo [122], a bridging coagulation of clay particles by the $Al(OH)_{3(S)}$ can be represented in Figure 7.6.



Figure 7.6 A bridging mechanism for clay particles using precipitated aluminium hydroxide (after Amirtharajah and Tambo [122]).

Results for kaolin suspensions treated with HTAB and coagulants are shown in Figure 7.7 for 5 mg/L alum, Figure 7.8 for 5 mg/L ferric chloride and Figure 7.9 for 1 mg/L PAC, respectively. All figures show flocculation efficiencies for the 100 mg/L kaolin suspension to be higher than those for the 50 mg/L concentration. The efficiencies seem to be independent of HTAB concentrations in the range of 0-1 x 10^{-5} mol/L. It may be concluded that HTAB additions is not involved in the flocculation mechanism, which is dependent on coagulants dosed. The efficiency response for the ferric chloride addition gave the highest removal efficiency compared to the alum and PAC.

It is believed that kaolin flocs are formed by an adsorption mechanism at low concentrations of coagulant and high concentrations of solids. This view agrees with O'Melia and Dempsey [123] who claimed that kaolin suspensions at the neutral pH form flocs by an adsorption mechanism at the low concentrations of the alum addition and flocculate by a sweep floc mechanism at the high concentrations of alum.



Figure 7.7 Flocculation test of 50 mg/L and 100 mg/L kaolin suspensions each treated with 5 mg/L of alum and various concentrations of HTAB solutions.



Figure 7.8 Flocculation test of 50 mg/L and 100 mg/L kaolin suspensions each treated with 5 mg/L of ferric chloride and various concentrations of HTAB solutions.



Figure 7.9 Flocculation test of 50 mg/L and 100 mg/L kaolin suspensions each treated with 1 mg/L of PAC and various concentrations of HTAB solutions.

7.2.2 Wyoming bentonite suspensions

Removal efficiencies for 50 and 100 mg/L of Wyoming bentonite suspensions treated with alum, ferric chloride and polyaluminuim chloride (PAC), are shown in Figures 7.10 to 7.12, respectively. The initial pH of the suspensions was about 7.4 and the pH values of each final solution fell at increased coagulant concentration as presented in Figures 7.13 and 7.14.

The results show that flocculation efficiencies for the 50 mg/L concentration of Wyoming bentonite suspensions treated with all three coagulants also give values lower than those for the 100 mg/L concentration. Again, it is believed that as the clay suspension concentrations were increased, a decrease in interparticle distances obtained so more particle collisions occurred during the coagulation process i.e. a second order rate process.



Figure 7.10 Flocculation test of 50 mg/L and 100 mg/L Wyoming bentonite suspensions with alum solutions.



Figure 7.11 Flocculation test of 50 mg/L and 100 mg/L Wyoming bentonite suspensions with ferric chloride solutions.



Figure 7.12 Flocculation test of 50 mg/L and 100 mg/L Wyoming bentonite suspensions with PAC solutions.



Figure 7.13 pH of 50 mg/L Wyoming bentonite suspensions with various coagulants.



Figure 7.14 pH of 100 mg/L Wyoming bentonite suspensions with various coagulants.

Figure 7.10 shows the increase in flocculation efficiencies and both curves reach a plateau region in the range of 10-50 mg/L of alum but the efficiencies drop slightly when the alum concentrations are above 50 mg/L. It seems that the optimal alum concentrations are in this range. For the ferric chloride treatment shown in Figure

7.11, the optimal concentrations are likely to be in the range of 30-60 mg/L while Figure 7.12 shows the most effective treatment with PAC to be in the concentration range of 5-25 mg/L.

Compared to alum treatment, PAC gave higher flocculation efficiencies as described in the previous section and ferric chloride treatment produced removal efficiencies that were lower than those for either of the other coagulants.

Figures 7.15 to 7.17 show the effect of HTAB on the Wyoming bentonite suspensions treated with alum and ferric chloride at 5 mg/L concentration and PAC at 0.5 mg/L concentration.



Figure 7.15 Flocculation test of 50 mg/L and 100 mg/L Wyoming bentonite suspensions each treated with 5 mg/L of alum and various concentrations of HTAB.



Figure 7.16 Flocculation test of 50 mg/L and 100 mg/L Wyoming bentonite suspensions each treated with 5 mg/L of ferric chloride and various concentrations of HTAB.



Figure 7.17 Flocculation test of 50 mg/L and 100 mg/L Wyoming bentonite suspensions each treated with 0.5 mg/L of PAC and various concentrations of HTAB.

All results show flocculation efficiencies for the 100 mg/L suspensions to be higher than those for the 50 mg/L ones. With alum added at 5 mg/L, the efficiencies are likely to be independent of HTAB concentrations in the range of 0-1 x 10^{-5} mol/L. The efficiencies for suspensions treated with 5 mg/L of ferric chloride and 0.5 mg/L of PAC were increased with further addition of HTAB and reached efficiencies of about 95% at HTAB concentration of 1 x 10^{-5} mol/L for both of the clay concentrations. This suggests that a HTAB concentration of 1 x 10^{-5} mol/L at least will control the flocculation efficiency of Wyoming bentonite suspensions treated with a low concentration of either ferric chloride or PAC solutions.

7.3 Effect of coagulants on floc sizes in flocculation tests

The effects of the three coagulants on the sizes of kaolin and Wyoming bentonite flocs are shown in Figures 7.18 and 7.19 for clay concentrations of 50 mg/L and 100 mg/L, respectively. Observations from the experiments showed that kaolin formed opaque flocs while Wyoming bentonite produced translucent flocs with a floc diameter up to about 100 μ m as shown in Figure 7.20. However, both Figures 7.18 and 7.19 show that kaolin suspensions treated with coagulants gave maximum mean chord lengths (diameters) in the range of 40-60 μ m and the maximum mean diameters for the Wyoming bentonite flocs are in the range of 10-20 μ m. This suggests that the kaolin flocs are stronger than the Wyoming bentonite flocs. The floc break-up tests in section 7.5 and flotation tests will support this conclusion.

For the kaolin flocs, the optimal mean diameters were obtained in the concentration range of 40-60 mg/L for alum and ferric chloride treatment and in the range of 10-40 mg/L with PAC. This supported the results obtained from the flocculation tests reported in section 7.2. However, the size measurements of the Wyoming bentonite flocs could not be reconciled quite so easily with the results of the flocculation experiments.



Figure 7.18 Mean chord lengths for 50 mg/L kaolin (KL) and Wyoming bentonite (WB) treated with various coagulants.



Figure 7.19 Mean chord lengths for 100 mg/L kaolin (KL) and Wyoming bentonite (WB) treated with various coagulants.

It is believed that the Wyoming bentonite flocs prepared in coagulant solutions are weaker than kaolin-coagulant flocs. This result is not fully understood but it may be noted that Wyoming bentonite (sodium bentonite) dispersed in tap water may change to be calcium bentonite. It is found that calcium bentonite can produce a gel structure giving floc sizes between three or four times greater than those in the sodium bentonite structure [124]. On the other hand, kaolin is generally considered to be nonexpandable clay dispersed in water. This agreed well with the observation from experiments that Wyoming bentonite, either dispersed in tap water or dosed with coagulants, formed translucent flocs with a fluffy structure that was broken easily. However, another contributory observation found that Wyoming bentonite flocs were able to reaggregate after suspensions were left to stand for a short time.



Figure 7.20 Wyoming bentonite-ferric chloride flocs showing the translucent structures.

7.4 Effect of interfacial forces on flocculation tests

7.4.1 Effect of zeta potential on flocculation tests

Generally, coagulation and flocculation occur when the zeta potentials of particles reduce into the range of ± 10 mV. However, the other forces such as hydrophobic ones may play an important role in some systems. Addition of surfactants to suspensions may control hydrophobic forces.

Zeta potential and coagulation diagrams are the major tools for predicting and describing the chemical conditions that effect coagulation. The zeta potentials of clay suspensions have been used by several workers [29-37] to explain flocculation efficiencies. For the alum coagulation diagram in Figure 2.3, the interaction of positive aluminium hydroxide and the negative colloid gives two points of zero zeta potential at pH values of 4.8 and 6.8 and good coagulation obtains normally at or near the point of zero charge.

The zeta potentials of clay suspensions diluted with tap water of high alkalinity are not a critical parameter in producing flocculation, a view which is also supported by flocculation modelling in the next section. At high ionic strength, electrostatic forces are normally short-range forces which become very weak at about 5-10 nm from a particle surface. This agreed with Gregory [108] who mentioned that flocculation occurred over a broad range as the ionic strength of suspensions was increased and less chemical was required to destabilise the particles and more needed to give restabilisation.

7.4.2 Flocculation modelling

In Chapter 6 the predictions of flocculation for clay suspensions treated with coagulants showed that there was no evidence of agglomeration because the free energies of material (1) in medium (3), ΔG_{i31}^T , gave positive values. A full explanation

is not available but it is possible to explain the flocculation results by using extended-DLVO theory. Clearly, the extended-DLVO theory is used normally to explain the flocculation of particles dosed with organic molecules, such as HTAB, which create hydrophobic forces.

The model obtained from the simulation programme of the extended-DLVO theory given in Appendix H can be used to describe the flocculation results in the previous section and some other details will also be discussed in Chapter 9. For two identical particles in water, generally, van der Waals forces always show negative values or attraction while electrostatic forces give the positive values or repulsion. Hydration forces are normally repulsive and generated by adsorbed hydrated cations such as sodium and potassium ions [108], while hydrophobic forces may be either positive or negative depending on the surface energy of particles. At high ionic strength (more than 1 mM), short-range repulsive hydration forces decreased exponentially over the range of 1.5-4 nm. The present results show that the hydration forces of clay particles agglomerated with coagulants were positive while those particles in high concentrations of HTAB exhibited attractive hydrophobic forces.

Figure 7.21 presents the results of modelling the kaolin suspension behaviour with and without HTAB added. The kaolin suspension diluted with tap water shows the secondary minimum in the total free energy, which can be responsible for the formation of weak aggregates. This result was supported by particle size measurements using a laser diffraction technique identifying the aggregates of the kaolin suspension prepared as described in section 5.3.1.

For HTAB additions in the range of 5×10^{-6} to 5×10^{-5} mol/L, the total free energies are altered at separation distances up to 18 nm but there are no effects on the total free energies when the separation distances are longer than about 18 nm. For separation distances between 0-18 nm, the total free energies were decreased with increasing HTAB concentrations due to the increases in a hydrophobic force (see more details in

Chapter 9). The mean particle sizes obtained using the Lasentec apparatus were slightly changed with increasing HTAB concentrations. It is believed that HTAB adsorption on the kaolin particles increases with increasing HTAB concentration but a particle size change was not identified because HTAB concentrations up to 5 x 10^{-5} mol/L may be too far from the isoelectric point of kaolin in HTAB (about 10^{-4} mol/L).



Figure 7.21 Modelling of 50 mg/L kaolin suspensions in various HTAB concentrations.

Figure 7.22 shows the results obtained from flocculation models for a kaolin suspension treated with either coagulants or HTAB. For coagulant additions, a secondary minimum was obtained at a separation distance of about 9 nm and the total free energies represented greater attractive forces when compared to the suspension without coagulant. This result suggests that kaolin suspensions treated with coagulants can form stronger aggregates more easily than without coagulants. Ferric chloride would give bigger flocs in comparison to alum and PAC solutions. The results were confirmed by floc breakup tests as described in the next section. The kaolin suspension dosed with ferric chloride produced the biggest flocs while the alum gave larger flocs in comparison to the PAC. For HTAB-coagulant additions, the secondary minimum occurs at the separation distance of about 6 nm, which is a lower distance than without HTAB, while the long-range forces are slightly lower than those

without HTAB. This suggests that kaolin suspensions treated with HTAB-coagulants can form aggregates more easily but that these are weaker than those obtained with coagulants only.



Figure 7.22 Modelling of 50 mg/L kaolin suspension in coagulant (40 mg/L of alum, 40 mg/L of ferric chloride and 10 mg/L of PAC) and HTAB-coagulant (HTAB at 1 x 10^{-5} mol/L dosed with each of 40 mg/L of alum, 40 mg/L of ferric chloride and 10 mg/L of PAC).

Figure 7.23 presents the results obtained from the modelling of a Wyoming bentonite suspension treated with and without HTAB. The Wyoming bentonite suspension diluted with tap water shows the secondary minimum, which can be responsible for the formation of weak aggregates. This result agreed well with the experimental finding of a gel structure for Wyoming bentonite aggregates as described in section 5.3.1 and discussed in section 7.3.

For HTAB additions in the range of 5×10^{-6} to 3×10^{-5} mol/L, the total free energies were attractive and changed from short-range to long-range when the HTAB concentrations were increased due to the increases in the hydrophobic forces (see more details in Chapter 9). The effect on mean particle sizes of suspensions as measured by the Lasentec apparatus of increasing HTAB concentrations demonstrates

an increase in the hydrophobic forces. Clearly, HTAB adsorption on Wyoming bentonite particles increases with increasing HTAB concentrations.

Parker and co-workers [125] and Yaminsky and co-workers [126] found that total forces on glass surfaces treated with HTAB at a concentration of 5 x 10^{-5} mol/L are attractive and these forces also showed much longer range and stronger than van der Waals forces.



Figure 7.23 Modelling of 50 mg/L Wyoming bentonite suspension with HTAB concentrations.

Figure 7.24 shows the results obtained from the flocculation model of the Wyoming bentonite suspension dosed with either coagulants or HTAB. For coagulant additions, the total free energies obtained from the flocculation model gave a secondary minimum at a separation distance of about 12 nm. This result suggests that the Wyoming bentonite suspensions treated with coagulants can form aggregates better than the Wyoming bentonite without chemical addition. For HTAB-coagulant additions, the total free energy curves show the secondary minimum slightly lower than those without HTAB at a separation distance of about 11 nm near the secondary minimum for the suspensions treated only with coagulants. This suggests that the
Wyoming bentonite suspensions treated with HTAB-coagulants can form aggregates that are slightly stronger and bigger than those obtained only with coagulants. Again, this result is supported by the floc breakup tests described in the next section.



Figure 7.24 Modelling of 50 mg/L Wyoming bentonite suspension in coagulant (40 mg/L of alum, 40 mg/L of ferric chloride and 10 mg/L of PAC) and HTAB-coagulant additions (HTAB 1 x 10^{-5} mol/L added to each of 40 mg/L alum, 40 mg/L ferric chloride and 10 mg/L PAC).

7.5 Floc breakup tests

The mean equilibrium floc size is defined as an average diameter of stable flocs and it is a function of coagulant dosage, agitation rate, pH and suspension characteristics [47]. This parameter is measured normally in floc breakage tests under the application of a shear gradient (see Appendix G for the calculation details of shear forces). The raw data for the mean floc sizes are given in Appendix C and the results of particle size distributions are presented in section 7.6.

7.5.1 Kaolin flocs

For the kaolin suspension treated with HTAB, the size differences between the kaolin flocs were not found using the particle size measurement apparatus (Lasentec) when

the shear gradients are increased i.e. there was no change in the signal from the Lasentec with respect to time after a shear gradient was changed. This result is in agreement with Jefferson [97] who found no flocculation in kaolin suspensions diluted with distilled water and treated with HTAB. The effects of shear gradients on kaolin with coagulants are shown in Figure 7.25 for kaolin-coagulant flocs and Figure 7.26 for kaolin-HTAB-coagulant flocs.



Figure 7.25 Effects of shear gradient on the size of kaolin-coagulant flocs.



Figure 7.26 Effects of shear gradient on the size of kaolin-HTAB-coagulant flocs.

Observations from the experiments showed that flocculated particles gave stable floc sizes under shear gradients for each test. This result agreed with Peng and Williams [47] who found that a breakage process and reaggregation were produced simultaneously in floc breakup tests.

According to equation (3.62), a floc strength coefficient (C_s) and an exponent (l_B) can be obtained from the intercept and slope of the relationship between a mean stable floc size (d_s) and shear gradient.

$$d_s = C_s G'_{s} \tag{3.62}$$

Table 7.1 shows the shear parameters, with the exponent in the range of -0.4 to -0.6. A statistical parameter (R^2) showed a good fit of the present results. The exponent values were supported by Tambo and Francois [43] and Muhle [127] who obtained similar values in the range of -0.1 to -0.5.

Table 7.1 Shear parameters of the kaolin flocs with various coagulants and HTAB surfactant.

Туре	coagulant concentration	l_B	C _s	R ²
	(mg/L)			
Kaolin in alum	40	-0.526	324.1	0.93
Kaolin in ferric chloride	40	-0.468	353.9	0.95
Kaolin in PAC	10	-0.604	368.0	0.98
Kaolin in HTAB* and alum	40	-0.525	263.7	0.99
Kaolin in HTAB* and FeCl ₃	40	-0.379	195.2	0.93
Kaolin in HTAB* and PAC	10	-0.579	330.0	0.99

* HTAB concentration is 1×10^{-5} mol/L.

7.5.2 Wyoming bentonite flocs

The effects of shear gradient on Wyoming bentonite flocs are shown in Figure 7.27 for Wyoming bentonite-HTAB flocs and Figure 7.28 for Wyoming bentonite-HTAB-coagulant flocs. For the Wyoming bentonite suspension dosed only with coagulants,

the particle size measurement apparatus (Lasentec) found no effect of the shear gradient on the size distribution of the Wyoming bentonite flocs. This suggests that the Wyoming bentonite-coagulant flocs are weaker than those of the kaolin-coagulant flocs and an explanation has been offered in the previous section.



Figure 7.27 Effects of shear gradient on the size of Wyoming bentonite-HTAB flocs.



Figure 7.28 Effects of shear gradient on the size of Wyoming bentonite-HTAB-coagulant flocs.

Table 7.2 shows the shear parameters with the exponent in the range of -0.1 to -0.7 for the Wyoming bentonite flocs. A statistical parameter (R^2) showed a poor fit for the Wyoming bentonite-HTAB flocs but a good result for the Wyoming bentonite-HTAB flocs.

Table 7.2 Shear parameters of the Wyoming bentonite flocs with various coagulants and HTAB surfactant.

Туре	HTAB concentration	l _B	C_s	R ²
	(mol/L)			
WB in HTAB	5 x 10 ⁻⁶	-0.414	86.1	0.89
WB in HTAB	1 x 10 ⁻⁵	-0.701	582.9	0.97
WB in HTAB	2 x 10 ⁻⁵	-0.378	314.2	0.87
WB in HTAB	3 x 10 ⁻⁵	-0.173	166.3	0.85
WB in HTAB	5 x 10 ⁻⁵	-0.146	162.9	0.82
WB in HTAB + alum 40 mg/L	1 x 10 ⁻⁵	-0.439	102.7	0.94
WB in HTAB + FeCl ₃ 40 mg/L	1 x 10 ⁻⁵	-0.583	254.9	0.99
WB in HTAB + PAC 10 mg/L	1 x 10 ⁻⁵	-0.352	67.0	0.97

7.6 Effect of shear on size distributions of flocs

7.6.1 Kaolin

Grade distributions of kaolin-alum floc sizes are shown in Figure 7.29. Particle counts were increased when the agitator speeds were increased from 100 rpm to 150 and 200 rpm, respectively. The results also indicate that flocs with diameters greater than 100 μ m that were present at 100 rpm were reduced to smaller flocs when the speeds were increased. The mean diameters of kaolin-alum flocs are 37.3, 29.6 and 21.0 μ m for the shear gradients at 100, 150 and 200 rpm, respectively. The effect of the shear gradients showed a similar result on the grade distribution of kaolin-ferric chloride flocs in Figure 7.30 and kaolin-PAC flocs in Figure 7.31.



Figure 7.29 Effects of shear gradient on the size distribution of the kaolin-alum flocs (at alum concentration of 40 mg/L).



Figure 7.30 Effects of shear gradient on the size distribution of the kaolin-FeCl₃ flocs (at FeCl₃ concentration of 40 mg/L).



Figure 7.31 Effects of shear gradient on the size distribution of the kaolin-PAC flocs (at PAC concentration of 10 mg/L).

For an HTAB addition of 1×10^{-5} mol/L, the mean diameters of kaolin flocs produced with HTAB and coagulants seem to be slightly smaller than those of kaolin-coagulant flocs as shown in Figures 7.32 to 7.34. In comparison to the kaolin suspension treated only with coagulants, the particle counts for the kaolin-HTAB-coagulant flocs are greater. This suggests that the kaolin-HTAB-coagulant flocs are weaker than the flocs formed without HTAB addition. The total free energies estimated in the flocculation model supported this result.



Figure 7.32 Effects of shear gradient on the size distribution of the kaolin-HTABalum flocs (at HTAB concentration of 1×10^{-5} mol/L and alum concentration of 40 mg/L).



Figure 7.33 Effects of shear gradient on the size distribution of the kaolin-HTAB-FeCl₃ flocs (at HTAB concentration of 1 x 10^{-5} mol/L and FeCl₃ concentration of 40 mg/L).



Figure 7.34 Effects of shear gradient on the size distribution of the kaolin-HTAB-PAC flocs (at HTAB concentration of 1 x 10^{-5} mol/L and PAC concentration of 10 mg/L).

Figures 7.35 and 7.36 show that HTAB additions in the concentration range of 5 x 10^{-6} to 1 x 10^{-5} mol/L have no effect on the size distributions of the kaolin suspension. However, the size distribution is likely to change when the HTAB concentrations increase up to 5 x 10^{-5} mol/L as shown in Figures 7.37 and 7.38. This result also supports the explanation of the increase in flocculation efficiencies for the kaolin suspension dosed with HTAB solutions because of the increases in the hydrophobic forces.



Figure 7.35 Effects of shear gradient on the size distribution of the kaolin-HTAB flocs (at HTAB concentration of 5×10^{-6} mol/L).



Figure 7.36 Effects of shear gradient on the size distribution of the kaolin-HTAB flocs (at HTAB concentration of 1×10^{-5} mol/L).



Figure 7.37 Effects of shear gradient on the size distribution of the kaolin-HTAB flocs (at HTAB concentration of 2×10^{-5} mol/L).



Figure 7.38 Effects of shear gradient on the size distribution of the kaolin-HTAB flocs (at HTAB concentration of 5×10^{-5} mol/L).

7.6.2 Wyoming bentonite

Grade distributions of Wyoming bentonite-HTAB flocs are shown in Figures 7.39 to 7.43. Again, particle counts rose when the agitator speeds were increased from 100 rpm to 250 rpm and flocs with diameters greater than 100 μ m that were present at 100 rpm were reduced to small flocs when the speeds were increased.



Figure 7.39 Effects of shear gradient on the size distribution of the Wyoming bentonite-HTAB flocs (at HTAB concentration of 5×10^{-6} mol/L).



Figure 7.40 Effects of shear gradient on the size distribution of the Wyoming bentonite-HTAB flocs (at HTAB concentration of 1×10^{-5} mol/L).



Figure 7.41 Effects of shear gradient on the size distribution of the Wyoming bentonite-HTAB flocs (at HTAB concentration of 2×10^{-5} mol/L).



Figure 7.42 Effects of shear gradient on the size distribution of the Wyoming bentonite-HTAB flocs (at HTAB concentration of 3×10^{-5} mol/L).



Figure 7.43 Effects of shear gradient on the size distribution of the Wyoming bentonite-HTAB flocs (at HTAB concentration of 5×10^{-5} mol/L).

7.7 Summary

Alum concentrations of 40 mg/L, ferric chloride 40 mg/L and PAC 10 mg/L were the selected coagulant dosages to be used in flotation tests. For the clay-HTAB-coagulant system, a HTAB concentration of 1 x 10^{-5} mol/L showed the optimum effect on flocculation efficiencies and this concentration will also be used in the flotation tests. The particle size measurements gave results which helped to explain the flocculation phenomena and similar measurements were employed to investigate the effect of shear gradients on floc sizes. Clearly, the hydrophobic forces were increased with increasing HTAB concentrations while the hydration effects occurred upon the addition of coagulants to the suspensions. Finally, a flocculation model using the extended-DLVO theory produced an explanation for the experimental results.

Chapter 8

Results and discussion: Flotation tests

8.1 Introduction

This chapter discusses the results obtained from the flotation tests on clay suspensions treated with chemicals. The semi-continuous flotation equipment described in Chapter 5 was used at a suspension flow rate of 2 L/min and the results are given in Appendix C. Interfacial forces including free energy terms will be used to interpret the flotation test results for both kaolin and Wyoming bentonite suspensions. Finally, grade efficiencies and diagrams of bubbles and flocculated particles are used to describe flotation mechanisms.

8.2 Flotation tests

The flotation rig contained a pressure vessel, an air supply unit, a feed pump, a flocculation unit, a high pressure pump, a flotation column and a holding tank. The holding tank was connected between a rectangular separation box fixed on the top of the column and an effluent pipe. The tank was able to provide enough suspension for a 30 minute test at a flow rate of 2 L/min. Flotation efficiencies were calculated from turbidity measurements of treated effluent compared to initial suspension (see more detail in section 8.2.3). A 50 mg/L Wyoming suspension dosed with 1×10^{-5} mol/L HTAB and 10 mg/L PAC was tested at retention times of 10 and 30 minutes in the recycle ratio range of 10-30%. The effect of the retention times on flotation efficiencies is given in Figure 8.1 showing little difference between two tested runs. Observations from the experiments showed that floated agglomerates separated clearly at the top of the rectangular box and some settling flocs remained in a bottom part of the holding tank. It may be concluded that the retention time at 10 minutes is good enough to use for further flotation tests on both kaolin and Wyoming suspensions dosed with either HTAB or coagulant solutions.



Figure 8.1 Wyoming bentonite treated with $1 \ge 10^{-5}$ mol/L HTAB and 10 mg/L PAC for retention times (RT) at 10 and 30 minutes.

8.2.1 Kaolin suspensions

Effects of recycle ratios on flotation efficiencies based on turbidity measurements for kaolin suspensions at a concentration of 50 mg/L treated with HTAB solutions in the concentration range of 0 to 2 x 10^{-5} mol/L are shown in Figure 8.2. Removal efficiencies are increased with increasing both recycle ratios from 10 to 40 % and HTAB solution concentrations. Clearly, the hydrophobicity of clay particles is increased when the surfactant concentrations are increased [106, 107].

When cationic surfactants are dosed into clay suspensions, an adsorption mechanism may occur involving an electrostatic force between negatively charged particles and positively charged molecules such as HTAB, which provides surfactant hydrocarbon tails to the bulk solution. It is believed that initial adsorption is probably complete within less than a second and is followed by a slow diffusion of the oppositely charged counterions as an ion pair from the particle surfaces to the bulk solution [128]. As well as eliminating electrical repulsion between the particles, an attraction could be introduced as a result of the hydrophobic forces.



Figure 8.2 Flotation efficiency against recycle ratio for the 50 mg/L kaolin suspensions dosed with HTAB in the concentration range of 0-2x 10^{-5} mol/L.

For kaolin-HTAB solution, it is believed that HTAB molecules initially adsorb onto kaolin surfaces via an ammonium polar head group. Clearly, kaolin suspensions did not form flocs in low concentrations of HTAB solutions as described in the previous chapter. Because kaolin flocs are not formed with HTAB at low concentrations, when the recycle ratios were increased, not only were more bubbles introduced into the flotation column but also a dilution effect occurred as a result of the increase in the flotation efficiencies. Pictures of kaolin particles adhering to bubbles in section 8.6 will confirm the removal results.

Jar test experiments showed that kaolin flocs were formed with each coagulant solution. The effect of coagulants on the removal efficiencies is exhibited in Figure 8.3. An optimum condition for the kaolin suspensions treated with coagulants is obtained at 10% recycle ratio where a 10 mg/L PAC solution gives the highest efficiency while alum and ferric chloride solutions show lower comparable results. This is because the zeta potential for suspensions treated with PAC has a lower value and the hydrophobic force is more attractive when compared to those treated with alum and ferric chloride. When the recycle ratios were increased to more than 10%,

the removal efficiencies were decreased. This may be attributed to the kaolincoagulant flocs being destroyed by increasing shear forces due to the injection of saturated water. This factor was evaluated using floc break-up tests as described in Chapter 7.



Figure 8.3 Flotation efficiency against recycle ratio for the 50 mg/L kaolin suspensions treated with 40 mg/L alum, 40 mg/L ferric chloride and 10 mg/L PAC solutions, respectively.

For the kaolin suspensions treated with HTAB at a concentration of 1×10^{-5} mol/L together with each coagulant, the effect of hydrophobic forces on the flotation efficiencies is shown in Figure 8.4. The flotation efficiencies are increased with increasing recycle ratios, which reached an optimum value at about 15% recycle ratio. However, the efficiencies drop slightly when the recycle ratios are increased up to 30%.

In comparison to Figure 8.3, however, the flotation efficiencies for the suspension treated with HTAB-coagulants in the recycle ratio range of 6-12% have lower values. This result is not fully understood but it is believed that particle capture is a controlling factor when the suspensions are treated with coagulants. This is because the particle sizes of the kaolin suspensions treated with coagulants show greater

values compared to those treated with HTAB-coagulants at low shear rate. However, for recycle ratio over 15%, flotation efficiencies for the suspension treated with HTAB-coagulants are higher than those treated only with coagulants. It is believed that both particle sizes and hydrophobic forces are main parameters for HTAB-coagulant system. When flocs are broken, an adsorption mechanism may be dominant, which affects flotation efficiencies as well as the result obtained from the suspension treated only with HTAB.

A major parameter is the hydrophobicity between bubbles and kaolin flocs which is increased due to a decrease in polar free energies, ΔG_{132}^{AB} , as given in Tables 6.10 to 6.12. This hypothesis was supported by the particle size measurements as described in Chapter 7 showing that the kaolin flocs gave similar sizes at high shear rate in suspensions with coagulants dosed with and without HTAB solutions. This suggests that capture efficiencies in both conditions should have similar results while an attachment efficiency resulting from the hydrophobic forces is increased by HTAB addition.



Figure 8.4 Flotation efficiency against recycle ratio for the 50 mg/L kaolin suspensions treated with 1×10^{-5} mol/L HTAB and 40 mg/L alum, 40 mg/L ferric chloride and 10 mg/L PAC, respectively.

8.2.2 Wyoming bentonite suspensions

Effects of recycle ratios on flotation efficiencies for 50 mg/L Wyoming bentonite suspensions treated with HTAB solutions in the concentration range of 0 to 5 x 10^{-5} mol/L are shown in Figure 8.5. Three cases may be discerned. At low HTAB concentrations, 0 and 1 x 10^{-6} mol/L, the efficiencies increase with increasing recycle ratios from 10 to 30 %. It is believed that dilution is a major effect in these HTAB solutions due to the small size of Wyoming-HTAB flocs formed. When HTAB concentrations increase to the range of 5 x 10^{-5} mol/L, the efficiencies show the maximum removal at about 10% recycle ratio. Again, the hydrophobicity of clay particles is increased when the surfactant concentrations are increased, which produces not only bigger and stronger flocs but also increasing collision efficiencies between particles and bubbles.



Figure 8.5 Flotation efficiency against recycle ratio for the 50 mg/L Wyoming bentonite suspensions treated with HTAB solutions in the concentration range of 0-5x 10^{-5} mol/L.

At high concentrations of HTAB solutions, 3×10^{-5} to 5×10^{-5} mol/L, the flotation experiments give excellent results at about 99.9% removal in the recycle ratio range of

0-30%. Once again these results show the influence of strong hydrophobicity when HTAB solutions are used to deal with Wyoming bentonite suspensions. Because of high floc strength and strong hydrophobic forces, when the recycle ratios are increased up to 30%, the dissipating energy of the injected saturated water is not enough to break the flocs. A photograph of Wyoming bentonite flocs and bubbles shown in section 8.6 supports these results.

The effect of coagulants on the flotation efficiencies for the Wyoming bentonite suspensions is shown in Figure 8.6. The optimum condition for treatment with coagulants is produced at 10% recycle ratio with alum and ferric chloride at a concentration of 40 mg/L while a flat line of flotation efficiencies is exhibited with 10 mg/L PAC in the recycle ratio range of 6-30%. The effect of coagulants in this work showed low flotation efficiencies for Wyoming bentonite suspensions with coagulants. This may be attributed to the Wyoming bentonite-coagulant flocs being destroyed by an increase in shear forces due to the injection of further saturated water. The strength of the Wyoming bentonite-coagulant flocs, described in section 7.5.2, showed a decrease in floc sizes with increasing shear gradients.



Figure 8.6 Flotation efficiency against recycle ratio for the 50 mg/L Wyoming bentonite suspensions treated with 40 mg/L alum, 40 mg/L ferric chloride and 10 mg/L PAC solutions, respectively.

The strength of the flocs can be improved by increasing hydrophobic forces by surfactant additions. Figure 8.7 shows the flotation efficiencies for the Wyoming bentonite suspensions treated with 1×10^{-5} mol/L HTAB as well as each coagulant in the recycle ratio range of 6-30%. Again, the efficiencies show an optimum condition at 10% recycle ratio and the effect of HTAB solutions on the removal efficiencies gives a good improvement for PAC, increasing the efficiencies from about 15% up to 90% while comparable values for either alum or ferric chloride are about 60%. The great improvement for PAC-HTAB addition is not fully understood but it may result from a decrease in zeta potentials for this condition lower than those treated with alum-HTAB and ferric chloride-HTAB.

When the recycle ratios were increased to more than 10%, the removal efficiencies decreased. This may occur because of floc breakage again due to increased shear forces. It seems that the flotation of Wyoming bentonite is most efficient with only HTAB present at high concentration. Coagulant is not necessary.



Figure 8.7 Flotation efficiency against recycle ratio for the 50 mg/L Wyoming bentonite suspensions treated with 1×10^{-5} mol/L HTAB and 40 mg/L alum, 40 mg/L ferric chloride and 10 mg/L PAC, respectively.

8.2.3 Effect of particle count and suspended solid measurements on flotation tests

To determine flotation efficiencies, three techniques, turbidity (NTU), particle counts using the Lasentec apparatus, and suspended solid measurements, were used in some experiments with kaolin and Wyoming bentonite suspensions dosed with chemicals. Figures 8.8 and 8.9 show the flotation efficiencies for the kaolin suspensions with HTAB treated with either alum or ferric chloride at a concentration of 40 mg/L. The particle count technique gave flotation efficiencies higher than two other methods which showed similar results.

The reason for the higher values obtained by the particle count technique is not fully understood but it is likely to be because of the reaggregation of small flocs when a sample has been left to stand for few minutes before the particle size distribution is measured. The "reaggregation of particle" explanation is confirmed by the size distribution results as shown in section 8.4. Another contributory factor may be that the Lasentec equipment cannot detect particles having sizes less than 1 μ m which would give an increase in the calculated efficiencies. It is believed that the small particles (less than 1 μ m) are more difficult to remove by the flotation process [49].



Figure 8.8 Flotation efficiencies for the 50 mg/L kaolin suspensions treated with 1 x 10^{-5} mol/L HTAB and 40 mg/L alum, measured using turbidity (NTU), particle count (PC) and suspended solid (SS) techniques.



Figure 8.9 Flotation efficiencies for the 50 mg/L kaolin suspension treated with 1 x 10^{-5} mol/L HTAB and 40 mg/L ferric chloride, measured using turbidity (NTU), particle count (PC) and suspended solid (SS) techniques.

The flotation efficiencies for Wyoming bentonite suspensions dosed with HTAB and either alum or ferric chloride at a concentration of 40 mg/L are shown in Figures 8.10 and 8.11, respectively.



Figure 8.10 Flotation efficiencies for the 50 mg/L Wyoming bentonite suspensions treated with 1 x 10^{-5} mol/L HTAB and 40 mg/L alum, measured using turbidity (NTU), particle count (PC) and suspended solid (SS) techniques.

Again, the results show that the particle count technique gives flotation efficiencies higher than two other methods. Surprisingly, the efficiencies measured by the particle count technique as shown in Figure 8.11 give a greatly different result compared to both other methods.

It may be concluded that turbidity measurement is the most powerful technique for a determination of flotation efficiencies. The main advantages of the turbidity method are that it is easy and quick to use. Experimental results showed that both turbidity and suspended solid measurements gave similar removal efficiencies for the clay suspensions treated with HTAB and/or coagulants.



Figure 8.11 Flotation efficiencies for the 50 mg/L Wyoming bentonite suspensions treated with 1 x 10^{-5} mol/L HTAB and 40 mg/L ferric chloride, measured using turbidity (NTU), particle count (PC) and suspended solid (SS) techniques.

8.2.4 Effect of anionic surfactants on flotation efficiency

Figure 8.12 shows the effect of sodium dodecyl sulphate (SDS), an anionic surfactant, in the presence of 10 mg/L PAC solution on flotation efficiencies. At 10% recycle ratio, the efficiencies of Wyoming bentonite suspensions with 10^{-5} mol/L SDS are higher than with 10^{-6} mol/L solution. This suggests that hydrophobic forces are increased when surfactant concentrations are increased. However, the effect of

hydrophobicity on efficiencies is reduced when recycle ratios are increased from 10% to 30%. In a comparison with PAC-HTAB treatment, efficiencies for the Wyoming bentonite suspensions treated with 10⁻⁵ mol/L SDS and 10 mg/L PAC give lower values as shown in Figure 8.13. This may be due to repulsion forces created between negatively charged clay particles and the anionic surfactant, SDS.



Figure 8.12 Flotation efficiencies for the 50 mg/L Wyoming bentonite suspensions treated with either 1 x 10^{-5} mol/L or 1 x 10^{-6} mol/L sodium dodecyl sulphate (SDS) and 10 mg/L PAC.

The mechanisms of flotation using anionic surfactants were investigated by Rutland and Pugh [129] who summarised possible mechanisms in a flotation deinking process using fatty acids, such as oleic and stearic acids, dosed with calcium chloride solutions. Three possible mechanisms for the removal of negatively charged ink particles using negatively charged fatty acid collectors may occur. Firstly, direct calcium ion bridging; both particles and collectors are bridged by calcium ions with hydrocarbon tails of the fatty acids turning into the bulk solution and adhering to the air bubbles. Secondly, calcium soap precipitation; heterocoagulation or micro encapsulation may form between calcium soap precipitates and ink particles before attachment to the air bubbles. Finally, calcium ion destabilisation mechanisms; the ink particles are destabilised by calcium ions, and the positively charged aggregates are adsorbed by negatively charged fatty acids before adhering to the air bubbles.



Figure 8.13 Flotation efficiencies for the 50 mg/L Wyoming bentonite suspensions treated with either 1×10^{-5} mol/L HTAB or 1×10^{-5} mol/L SDS and 10 mg/L PAC.

Following Rutland and Pugh [129], flotation mechanisms for clay particles with HTAB solution and/or coagulants will be described further in section 8.7.

8.3 Effect of interfacial forces on flotation efficiency

8.3.1 Effect of zeta potential on flotation efficiency

In the absence of surfactants, flotation may occur at or near the point of zero charge. However, a hydrophobic force is an important parameter for suspensions treated with surfactants as described previously.

The effects of zeta potentials on flotation processes have been reported by several workers [11, 13, 14, 16, 17]. A simple model as described in Chapter 4 suggested that a flotation efficiency depended on the particle diameter and the product of the electromobilities of both particles and bubbles. Jefferson [97] claimed that maximum

flotation efficiencies ocurred near the point of zero charge for both kaolin and Wyoming bentonite suspensions diluted with distilled water and treated with three surfactant solutions, HTAB, TTAB and DTAB. However, the efficiencies for both clay suspensions dosed with alum and ferric chloride were different. For kaolin solutions, the optimum efficiency is in the zeta potential range of 10-20 mV while the Wyoming bentonite solutions show maximum efficiencies in the zeta potential range of 0-34 mV. This suggests that zeta potentials may not to be a controlling factor for a treatment with coagulants.

It may be concluded that the zeta potentials of clay suspensions diluted with high alkalinity tap water are not critical parameters. Two other forces, van der Waals and hydrophobic, are expected to combine with the electrostatic force as described in Chapter 4 and in the next section.

8.3.2 Effect of van der Waals and hydrophobic forces on flotation efficiency

As shown in Tables 6.9 to 6.12 ΔG_{132}^T gave negative values showing that agglomerations between bubbles and clay suspensions treated with chemicals were possible. For two identical particles (1) in water (3) van der Waals forces, ΔG_{131}^{LW} , always have negative values, implying attraction, while the free energy of particles (1) and bubbles (2) in solution (3), ΔG_{132}^{LW} , may represent either an attractive or repulsive force. The extended-DLVO theory showed that van der Waals forces ΔG_{132}^{LW} were repulsive while hydrophobic and most electrostatic forces were attractive.

The repulsive van der Waals forces were decreased with increasing surfactant concentrations. This agreed with Yoon and Mao [74] who claimed that the van der Waals forces were changed from repulsive to attractive by an increase in surfactant concentrations. In the present work the Hamaker constants, A_{132} , as given in Table 6.13 were all negative, which suggested that the van der Waals forces were repulsive.

The polar free energies between particles and air bubbles in solutions, ΔG_{132}^{AB} , as shown in Tables 6.9 to 6.13 gave negative values for all tests. These free energies were reduced with increasing HTAB concentrations. In other words, hydrophobic forces are increased by further additions of HTAB solution. This increase in hydrophobic forces due to further additions of surfactant concentrations was noted by several other researchers [106, 107].

Flotation mechanisms for clay suspensions dosed with surfactants are not fully understood but it is believed that adsorption of the surfactant molecules on both particles and bubbles occurs simultaneously during an operation. On bubble surfaces, the adsorption mechanism is the usual one with surfactant molecules orienting the hydrocarbon tails into the bulk volume of the bubbles and leaving the polar head groups on the bubble surfaces. On the other hand, the adsorption mechanism for surfactant molecules on particle surfaces is a neutralisation process between the particles and the polar head group molecules, which orients the hydrocarbon tails into the bulk solution. The results of zeta potential tests suggest that the bubbles require less surfactant molecules than the particles to reverse the charges from negative to positive.

8.4 Effect of floc size on flotation efficiency

8.4.1 Kaolin suspensions

Figures 8.14 and 8.15 show size distributions for kaolin suspensions in HTAB solutions at concentrations of 1×10^{-6} mol/L and 1×10^{-5} mol/L, respectively.

The effect of recycle ratios on flotation efficiencies is shown clearly when HTAB solution concentrations are increased from 1×10^{-6} mol/L to 1×10^{-5} mol/L. The particle counts of treated effluents are decreased with an increase in recycle ratios. This suggests that hydrophobicity and a dilution effect are major parameters on the removal of suspensions which form very small flocs such as kaolin treated with HTAB solutions.



Figure 8.14 Effect of recycle ratios on size distribution for the kaolin suspensions with 1×10^{-6} mol/L HTAB.



Figure 8.15 Effect of recycle ratios on size distribution for the kaolin suspensions with 1×10^{-5} mol/L HTAB.

When the kaolin suspensions are dosed with coagulants, the particle sizes are increased as shown in Figures 8.16 to 8.18 for alum, ferric chloride and PAC solutions, respectively.



Figure 8.16 Effect of recycle ratios on size distribution for the kaolin suspensions treated with 40 mg/L alum.



Figure 8.17 Effect of recycle ratios on size distribution for the kaolin suspensions treated with 40 mg/L ferric chloride.

The results show that the particle counts of the treated effluents are the lowest at about 10 % recycle ratio. This suggests that the optimum recycle ratio for kaolin suspensions treated with coagulants using a flotation process is at about 10%. In the case of low removal efficiencies, some measurements such those on kaolin suspensions treated with 40 mg/L alum at 12% recycle ratio show greater particle sizes. This may be due to reaggregation of small particles to form big flocs when samples have been left to stand for few minutes before the measurements are made.



Figure 8.18 Effect of recycle ratios on size distribution for the kaolin suspensions treated with 10 mg/L PAC.

Figures 8.19 to 8.21 show the particle size distribution for the kaolin suspensions treated with HTAB solutions at a concentration of 1×10^{-5} mol/L as well as alum, ferric chloride and PAC, respectively.



Figure 8.19 Effect of recycle ratios on size distribution for the kaolin suspensions with 1×10^{-5} mol/L HTAB and treated with 40 mg/L alum.

The results also show that the particle counts of treated effluents are the lowest at 10 % recycle ratio and the reaggregation is still observed at low removal efficiencies.



Figure 8.20 Effect of recycle ratios on size distribution for the kaolin suspensions with 1×10^{-5} mol/L HTAB treated with 40 mg/L ferric chloride.



Figure 8.21 Effect of recycle ratios on size distribution for the kaolin suspensions with 1×10^{-5} mol/L HTAB treated with 10 mg/L PAC.

8.4.2 Wyoming bentonite suspensions

Figures 8.22 and 8.23 show size distributions for Wyoming bentonite suspensions with and without 1 x 10^{-6} mol/L HTAB solution. Very low removal efficiencies are evident in the recycle ratio range of 8-14%.



Figure 8.22 Effect of recycle ratios on size distribution for the Wyoming bentonite suspensions.



Figure 8.23 Effect of recycle ratios on size distribution for the Wyoming bentonite suspensions with 1×10^{-6} mol/L HTAB.

The flotation efficiencies are increased greatly when HTAB concentrations are increased as shown in Figure 8.24.



Figure 8.24 Effect of recycle ratios on size distribution for the Wyoming bentonite suspensions with 3×10^{-5} mol/L HTAB.

Figures 8.25 and 8.26 show size distributions for the Wyoming bentonite suspensions treated with HTAB at a concentration of 1×10^{-5} mol/L as well as alum and ferric chloride at a concentration of 40 mg/L, respectively.



Figure 8.25 Effect of recycle ratios on size distribution for the Wyoming bentonite suspensions with 1×10^{-5} mol/L HTAB and 40 mg/L alum solutions.

The results show that particle counts obtained from treated water have the lowest values at 10 % recycle ratio.



Figure 8.26 Effect of recycle ratios on size distribution for the Wyoming bentonite suspensions with $1 \ge 10^{-5}$ mol/L HTAB and 40 mg/L ferric chloride solutions.

8.5 Grade efficiencies of flotation tests

8.5.1 Kaolin suspensions

At the 10% recycle ratio grade efficiencies for kaolin suspensions dosed with HTAB concentrations in the range of 1×10^{-6} to 1×10^{-5} mol/L, which do not form flocs, give minimum values in the floc size range of 10-20 µm as shown in Figure 8.27. This may be compared to a single collector collision model presented by Edzwald and coworkers [51, 87, 88] who found that the minimum efficiency is at a particle size of 1 µm rather than the 10 µm exhibited in Figure 8.27. This result is not fully understood but it may be noted that the single collector collision model includes only Brownian and hydrodynamic forces excluding electrostatic, van der Waals and hydrophobic forces, which are proportional to particle radius. If these forces were introduced into the single collector collision model, the flotation efficiency would rise due to an increase in attractive forces between bubbles and particles. However, this hypothesis needs to be tested in further work.



Figure 8.27 Grade efficiency at 10% recycle ratio for unflocculated kaolin suspensions treated with $1 \ge 10^{-6}$ mol/L HTAB.

For kaolin suspensions forming flocs with coagulants, the flotation efficiencies do not produce minimum values as shown in Figure 8.28.



Figure 8.28 Grade efficiency at 10% recycle ratio for flocculated kaolin suspensions treated with 40 mg/L alum, 40 mg/L ferric chloride and PAC 10 mg/L solutions.

The grade efficiency curves for kaolin suspensions treated with coagulants exhibit similar results in that the flotation efficiencies are independent of particle size in the range of 1-100 μ m. Clearly, kaolin particles with coagulants can form good flocs giving large agglomerates that are removed more easily by the flotation process.

8.5.2 Wyoming bentonite suspensions

Figure 8.29 shows grade efficiencies at 10% recycle ratio for Wyoming bentonite suspensions treated with HTAB solutions. The grade efficiencies for the suspensions with and without 1 x 10^{-6} mol/L HTAB are independent of particle size in the range of 1-30 µm while at a concentration of 3 x 10^{-5} mol/L HTAB the efficiency produced is nearly 99% in the particle size range of 1-500 µm.



Figure 8.29 Grade efficiency at 10% recycle ratio for the Wyoming bentonite suspensions treated with HTAB solutions.

The grade efficiencies at 10% recycle ratio for the Wyoming bentonite suspensions treated with either alum or ferric chloride together with HTAB solution are shown in Figure 8.30. Once again the grade efficiencies do not show a minimum value and both curves exhibit high removal efficiencies.


Figure 8.30 Grade efficiency at 10% recycle ratio for the Wyoming bentonite suspensions with 1 x 10^{-5} mol/L HTAB treated with 40 mg/L alum and ferric chloride.

8.6 Agglomeration pictures

The VCR system described in Chapter 5 was used to capture pictures of bubbleparticle agglomerates. Figure 8.31 shows pictures for kaolin suspensions treated with 1×10^{-5} mol/L HTAB. Unfortunately, these are not very clear but it is believed that the kaolin particles are attached in gaps between the bubbles as illustrated in Figure 8.35.



Figure 8.31 Aggregates of bubbles and kaolin particles treated with HTAB solution (one grid square is about 300 μ m).

For Wyoming bentonite suspension treated with 3 x 10^{-5} mol/L HTAB, agglomerates between bubbles and flocs are shown in Figures 8.32 to 8.34. Clearly, the bubbles are entrapped by Wyoming bentonite flocs.

Observations from experiments in the recycle ratio range of 6-40% also show that agglomerates do not occur below about a 30 cm height from the base of the flotation column hence this volume is defined as a mixing zone. This suggests that the saturated water and suspension streams have to be mixed completely before the agglomerates are produced above the mixing zone. Clearly, the fluid in the mixing zone flows vigorously so the sizes of weak flocs are reduced by an eddy effect creating from mixed streams. Beyond the mixing zone, the fluid in the flotation column flows smoothly where the agglomerates move up with a velocity higher than liquid flow. The bigger agglomerates will rise more quickly than small ones. According to a calculation as described in Appendix F, laminar flow was claimed at 40% recycle ratio for a suspension flow rate of 2 L/min.



Figure 8.32 Aggregates of bubbles and Wyoming bentonite suspensions treated with 3×10^{-5} mol/L HTAB solution at 8% recycle ratio, captured using the VCR system (one grid square is about 300 μ m).



Figure 8.33 Agglomerates of bubbles and Wyoming bentonite suspension, treated with 3×10^{-5} mol/L HTAB, captured using a camera.



Figure 8.34 Agglomerates of bubbles and Wyoming bentonite suspension, treated with 3×10^{-5} mol/L HTAB, captured using a camera.

8.7 Flotation mechanisms

The kaolin suspensions treated with HTAB solutions illustrated in Figure 8.31 are believed to comprise kaolin particles adhered to the bubble surfaces and produced by the simple mechanism shown in Figure 8.35. HTAB molecules are adsorbed on negatively charged particles under electrostatic forces. On the other hand, the HTAB molecules are adsorbed on the bubbles with the hydrocarbon tails inside the bubble volume and the positively charged ammonium groups are on the bubble surfaces. These adsorption phenomena have been described by many researchers [130-132].



Figure 8.35 The proposed flotation mechanism between spherical particles and bubbles treated with HTAB (for a picture of kaolin particles see Appendix I).

The mechanism causing the kaolin particles to adhere to the bubble surfaces is not fully understood but it is possible that the HTAB molecules may act to link particles and bubbles as shown in Figure 8.35. Three possible mechanisms may be proposed as follows: Firstly, particles without HTAB molecules attach to the adsorbed HTAB molecules on bubble surfaces by an electrostatic force. Secondly, particles with adsorbed HTAB molecules adhere to the bubble surfaces by a nonpolar force between the hydrocarbon tails and the bubbles. Finally, both mechanisms may occur simultaneously.

In the case of Wyoming bentonite suspensions with HTAB solutions, the proposed flotation mechanism is shown in Figure 8.36. Clearly, Figures 8.32 to 8.34 show bubbles entrapped by Wyoming bentonite-HTAB flocs giving large agglomerates in a flotation column. Again, it is believed that the HTAB molecules are adsorbed on negatively charged particles by electrostatic forces and on the bubbles by nonpolar forces.



Figure 8.36 The proposed flotation mechanism between bubbles and Wyoming bentonite suspensions treated with HTAB.

In the cases of kaolin and Wyoming bentonite suspensions dosed with coagulants, the proposed flotation mechanism is described in Figure 8.37. Observations from experiments showed that bubbles were entrapped by clay-coagulant flocs in a similar manner to the case of the Wyoming bentonite-HTAB solutions. However, the agglomerates produced were of a smaller size than those for the Wyoming bentonite suspensions dosed with HTAB at high concentrations. It seems that the Wyoming bentonite-HTAB flocs have greater strength and size than suspensions treated with coagulants, as described in section 7.5. Another contributory factor may be the high hydrophobic forces present between the Wyoming bentonite-HTAB surfaces.

The mechanism for bubbles attached to clay particles treated with coagulants is not fully understood but it is believed that a reduction of repulsive forces and an increase in floc sizes are major factors. A destabilisation process is often obtained when the zeta potential of particles is close to the point of the zero charge at which the particles can form flocs. Clearly, the greater floc sizes will have higher flotation efficiencies due to an increase in a collision efficiency between bubbles and flocculated particles [49].



Figure 8.37 The proposed flotation mechanism between bubbles and clay suspensions (both kaolin and Wyoming bentonite) treated with coagulants.

In the cases of kaolin and Wyoming bentonite suspensions dosed with HTAB as well as with each coagulant, a proposed flotation mechanism is shown in Figure 8.38.

Observations from experiments showed that bubbles were entrapped by clay-HTABcoagulant flocs. Again, the hydrophobic forces are increased with HTAB additions, which produces high removal efficiencies. In this mechanism it is believed that both metal hydroxide flocs and HTAB molecules can be adsorbed on the particle surfaces simultaneously by neutralisation processes. When the ammonium groups of the HTAB molecules are adsorbed, the hydrocarbon tails turn to the bulk solution and adhere to the bubbles due to presence of nonpolar forces.



Figure 8.38 The proposed flotation mechanism between bubbles and clay suspensions (both kaolin and Wyoming bentonite) treated with both coagulants and HTAB.

8.8 Summary

The results obtained from flotation tests for clay suspensions treated with chemicals in this work may be considered in two categories. Firstly, when particles form big flocs, the optimum efficiency is at a recycle ratio of about 10%. Secondly, when particles are likely to disperse in suspension, the flotation efficiencies are dependent on the recycle ratios. An addition of small amounts of surfactants can produce hydrophobic forces. Experimental results showed that an increase in the hydrophobic forces was able to improve the flotation efficiencies significantly. Finally, four proposed mechanisms for the clay suspensions treated with chemicals were introduced based on photographs of bubble-particle agglomerates taken inside a flotation column.

Chapter 9

Results and discussion: Flotation modelling

9.1 Introduction

This chapter discusses the results obtained from the flocculation and flotation models. The extended DLVO theory given in Appendix H is used to described the flocculation test results shown in Chapter 7 for clay suspensions treated with chemicals. The trajectory model described in Chapter 4 was modified by including a hydrophobic force and the relevant computer programme is shown in Appendix H3. The results obtained from flotation models are compared to experimental results described in Chapter 8.

9.2 Simulation of intermolecular forces for flocculation tests

Flocculation results for kaolin suspensions treated with and without chemicals, obtained from extended-DLVO theory predictions are shown in Figures 9.1 to 9.5.



Figure 9.1 Kaolin suspension diluted in tap water; ELEF is the electrostatic energy, VANF is the van der Waals energy, HYDF is the hydrophobic or hydration energy and TOTF is the total free energy.

Hydrophobic forces show repulsive short-range energies at separation distances up to 10 nm for suspensions dosed with HTAB up to 1×10^{-5} mol/L while the forces change to be attractive for 3 x 10^{-5} mol/L HTAB addition as shown in Figure 9.3. This indicates that HTAB additions can change the characteristics of particle surfaces due to the hydrophobic forces interacting between them.



Figure 9.2 Kaolin suspension treated with HTAB at a concentration of 1 x 10^{-5} mol/L.



Figure 9.3 Kaolin suspension treated with HTAB at a concentration of 3 x 10^{-5} mol/L.

When the hydrophobic forces were changed from repulsive to attractive, the total free energy for kaolin suspension at a concentration of HTAB 3 x 10^{-5} mol/L was

transformed to an attractive force, which indicated that kaolin can form flocs in this condition as described in Chapter 7.

Figure 9.4 and 9.5 show the effects on the free energies of kaolin suspensions treated with alum and with and without HTAB. It can be seen that HTAB addition at a concentration of 1 x 10^{-5} mol/L can reduce repulsive electrostatic and hydrophobic energies, which gives a secondary minimum value at lower separation distance and slightly lowers the total free energy.



Figure 9.4 Kaolin suspension treated with alum at a concentration of 40 mg/L.



Figure 9.5 Kaolin suspension treated with alum at a concentration of 40 mg/L and 1×10^{-5} mol/L HTAB.

For Wyoming bentonite diluted with tap water, electrostatic and hydrophobic energies are short range ones while the van der Waals energy is significant up to more than 25 nm as shown in Figure 9.6.



Figure 9.6 Wyoming bentonite suspension diluted in tap water.

When HTAB was dosed into the suspensions, the total free energies were reduced at separation distances up to 10 nm shown in Figure 9.7 and changed from repulsive to attractive at HTAB concentration of 3×10^{-5} mol/L as exhibited in Figure 9.8.



Figure 9.7 Wyoming bentonite suspension treated with HTAB at a concentration of 1×10^{-5} mol/L.



Figure 9.8 Wyoming bentonite suspension treated with HTAB at a concentration of 3×10^{-5} mol/L.

Figure 9.9 and 9.10 show the free energies for Wyoming bentonite suspensions treated alum and alum-HTAB, respectively. It can be seen that HTAB addition at a concentration of 1 x 10^{-5} mol/L can reduce repulsively hydrophobic energy, which gives a secondary minimum value at slightly lower total free energy and separation distance.



Figure 9.9 Wyoming bentonite suspension treated with alum at a concentration of 40 mg/L.



Figure 9.10 Wyoming bentonite suspension treated with 1 x 10^{-5} mol/L HTAB and alum at a concentration of 40 mg/L.

9.3 Simulation of intermolecular forces for flotation tests

The interfacial forces between bubbles and particles were simulated using the computer programme described in Appendix H2 using the zeta potentials and contact angle results obtained in Chapter 6.

The total free energies for kaolin suspensions treated with HTAB in the concentration range of 1 x 10^{-6} to 3 x 10^{-5} mol/L are shown in Figures 9.11 to 9.15. All total free energies are attractive at separation distances lower than 12 nm and they reverse to be positive (or repulsive forces) in the distance range of 12-15 nm depending on a further increase in HTAB concentrations and the results also give energy barrier, E_1 , values at distances of about 21 nm as shown in Table 9.1 (page 202). This suggests that an attachment between bubbles and particles may occur when a kinetic energy for the particle is higher than the energy barrier [74].

Hydrophobic forces are shown to be only short range forces for the suspensions treated with HTAB in the concentration range of 1×10^{-6} to 2×10^{-5} mol/L while the

van der Waals forces are long range repulsive forces, which decrease when HTAB concentrations are increased.



Figure 9.11 Interfacial forces for flotation tests obtained from a kaolin suspension treated with HTAB at a concentration of 1×10^{-6} mol/L.



Figure 9.12 Interfacial forces for flotation tests obtained from a kaolin suspension treated with HTAB at a concentration of 5×10^{-6} mol/L.



Figure 9.13 Interfacial forces for flotation tests obtained from a kaolin suspension treated with HTAB at a concentration of 1×10^{-5} mol/L.



Figure 9.14 Interfacial forces for flotation tests obtained from a kaolin suspension treated with HTAB at a concentration of 2×10^{-5} mol/L.

The total free energies for Wyoming bentonite suspensions treated with HTAB in the concentration range of 1 x 10^{-6} to 5 x 10^{-5} mol/L are shown in Figures 9.16 to 9.21. All total free energies are attractive at separation distances lower than about 15 nm and they reverse to be positive for longer distances and give energy barrier, E_1 , values at the distances about 22 nm as shown in Table 9.1.



Figure 9.15 Interfacial forces for flotation tests obtained from a kaolin suspension treated with HTAB at a concentration of 3×10^{-5} mol/L.



Figure 9.16 Interfacial forces for flotation tests obtained from a Wyoming bentonite suspension treated with HTAB at a concentration of 1×10^{-6} mol/L.

It is seen that van der Waals energies for Wyoming bentonite suspensions treated with HTAB are significant at long range. Although the Hamaker constants decreased with increasing HTAB concentrations, repulsive values were still obtained.



Figure 9.17 Interfacial forces for flotation tests obtained from a Wyoming bentonite suspension treated with HTAB at a concentration of 5×10^{-6} mol/L.



Figure 9.18 Interfacial forces for flotation tests obtained from a Wyoming bentonite suspension treated with HTAB at a concentration of 1×10^{-5} mol/L.

Hydrophobic and electrostatic energies have short range values. For HTAB in the concentration range of 1 x 10^{-6} to 2 x 10^{-5} mol/L, electrostatic energies have negative values and change to repulsive when HTAB concentrations are equal or higher than 3 x 10^{-5} mol/L.



Figure 9.19 Interfacial forces for flotation tests obtained from a Wyoming bentonite suspension treated with HTAB at a concentration of 2×10^{-5} mol/L.



Figure 9.20 Interfacial forces for flotation tests obtained from a Wyoming bentonite suspension treated with HTAB at a concentration of 3×10^{-5} mol/L.

Table 9.1 shows the maximum value of the total free energies obtained from results simulated shown in Appendix H. The maximum total free energies or energy barriers for kaolin suspensions are decreased with increasing HTAB concentrations in the range of 1×10^{-6} to 2×10^{-5} mol/L but the energy rises at the concentration of 3×10^{-5} mol/L. This suggests that an attachment efficiency is increased with further HTAB additions, which is a result discussed further in section 9.4.



Figure 9.21 Interfacial forces for flotation tests obtained from a Wyoming bentonite suspension treated with HTAB at a concentration of 5×10^{-5} mol/L.

Table 9.1 Energy barriers, E_1 , and separation distances at E_1 for kaolin and Wyoming bentonite suspensions treated with HTAB at various concentrations.

Clay	HTAB concentration	Energy barrier, E_1	Separation distance	
	(mol/L)	(J)	at E_1 (nm)	
kaolin	1 x 10 ⁻⁶	4.83×10^{-19}	19	
	5 x 10 ⁻⁶	4.51 x 10 ⁻¹⁹	21	
	1 x 10 ⁻⁵	4.26 x 10 ⁻¹⁹	21	
	2 x 10 ⁻⁵	3.64 x 10 ⁻¹⁹	22	
	3 x 10 ⁻⁵	3.76 x 10 ⁻¹⁹	22	
bentonite	1 x 10 ⁻⁶	$4.47 \ge 10^{-19}$	23	
	5 x 10 ⁻⁶	5.15 x 10 ⁻¹⁹	22	
	1 x 10 ⁻⁵	7.07 x 10 ⁻¹⁹	23	
	2 x 10 ⁻⁵	9.03 x 10 ⁻¹⁹	24	
	3 x 10 ⁻⁵	$1.10 \ge 10^{-18}$	23	
	5 x 10 ⁻⁵	1.52×10^{-18}	20	
			•	

For Wyoming bentonite suspensions, on the other hand, the maximum total free energies are increased with increasing HTAB concentrations. This result shows an increase in van der Waals forces because greater floc diameters have been formed.

9.4 Flotation model tests

Two flotation models, the particle trajectory and mixing zone, or penetration, models, have been proposed and compared to experimental results from a flotation rig. The trajectory model provides a good explanation of the results obtained from a reduction of floc sizes under flotation tests (increasing recycle ratios). The mixing zone model based on Matsui and co-workers' concept, shows a potential to describe flotation results obtained from a kaolin suspension treated with HTAB.

9.4.1 Trajectory model

The trajectory model, based on surface chemistry and hydrodynamic forces, was simulated using a computer programme as described in Appendix H3. The programme was calculated using the Runge Kutta technique. The reduction of floc sizes due to shear gradients was also included in the calculation in the case of Wyoming bentonite treated with HTAB. Table E4 in Appendix E showed the mean floc size obtained from the experiments described in Appendix G. Limiting trajectories obtained from the model shown in Appendix E6 are used to calculate efficiencies for kaolin and Wyoming bentonite suspensions treated with HTAB in the concentration range of 1×10^{-6} to 3×10^{-5} mol/L.

9.4.1.1 Kaolin suspensions

Simulated results for kaolin suspensions treated with $1 \ge 10^{-6}$ mol/L HTAB were compared to experimental results obtained from tests as shown in Figure 9.22. The agreement between theory and experiment is very good. With kaolin the particle size is not effected by shear gradients and efficiencies are increased with increasing recycle ratios.



Figure 9.22 Experimental results obtained from kaolin suspensions treated with HTAB at a concentration of 1×10^{-6} mol/L, compared to results obtained from the trajectory model.

For further HTAB concentration additions, however, the model shows efficiencies about 15% higher than the experimental ones as presented in Figures 9.23 to 9.25. These results are not fully understood but the discrepancy may be due to errors in the calculation of the number of bubbles. The deficit of bubbles between results obtained from experiments and calculation may be due to many factors such as assumption of water saturated efficiency for the saturator and a mean bubble size, and bubble coalescence. Jefferson [97] found that a mean bubble size was about 43 μ m and did not change with increasing HTAB concentrations up to about 5 x 10⁵ mol/L. In other words, if the water saturated efficiencies lower than the values shown in Figures 9.22-9.25. This implies that experimental efficiencies for kaolin suspensions treated with HTAB at a concentration of 1 x 10⁻⁶ mol/L have higher values than those obtained from the model. The underestimated results obtained from the model are not readily explained but may be due to the number of bubbles at low HTAB concentrations to be greater than those at high concentrations. However, it is clear that this problem is too

complicated to be explained with the available data so this hypothesis needs to be tested in further work.



Figure 9.23 Experimental results obtained from kaolin suspensions treated with HTAB at a concentration of 5 x 10^{-6} mol/L, compared to results obtained from the trajectory model.



Figure 9.24 Experimental results obtained from kaolin suspensions treated with HTAB at a concentration of 1×10^{-5} mol/L, compared to results obtained from the trajectory model.



Figure 9.25 Experimental results obtained from kaolin suspensions treated with HTAB at a concentration of 2 x 10^{-5} mol/L, compared to results obtained from the trajectory model.

9.4.1.2 Wyoming bentonite suspensions

Simulated flotation results compared to experimental results for Wyoming bentonite suspensions treated with HTAB in the concentration range of 1×10^{-6} to 3×10^{-5} mol/L are shown in Figures 9.26 to 9.29.

Particle size is not affected by shear gradients for the suspension treated with HTAB at 1×10^{-6} mol/L, and flotation efficiencies are increased with increasing recycle ratios. The results obtained from the model shows efficiencies higher by about 10% than the experimental results as shown in Figure 9.26. Again, this result may be due to the deficit of bubble numbers as discussed in the previous section.



Figure 9.26 Experimental results obtained from Wyoming bentonite suspensions treated with HTAB at a concentration of 1×10^{-6} mol/L, compared to results obtained from the trajectory model.



Figure 9.27 Experimental results obtained from Wyoming bentonite suspensions treated with HTAB at a concentration of 5 x 10^{-6} mol/L, compared to results obtained from the trajectory model.

For HTAB at 5 x 10^{-6} mol/L, the result obtained from the model shows a good correlation with increasing recycle ratios. The modelling values also have an optimum efficiency at 10% recycle ratio. A decrease in efficiencies when recycle ratios are increased to more than 10% is due to floc breakage, which indicates that the collision efficiency is reduced when floc sizes are decreased.

The model described in Appendix H was calculated using floc break-up data showing that floc diameters were decreased with increasing recycle ratios. Since it is difficult to determine a relationship between floc sizes and energy dissipation inside a flotation column, an indirect method is introduced using floc break-up data. The energy dissipation obtained from the suspension and saturated water streams were estimated from calculations as shown in Appendix G3 and compared to the power per unit volume values obtained from stirred tank tests shown in Appendix G2.

Figure 9.28 shows the experimental results obtained from Wyoming bentonite suspensions treated with HTAB at a concentration of 1×10^{-5} mol/L and compared to those from the model. Again, the difference is about 15%. On the other hand, the results shown in Figure 9.29 for a suspension treated with HTAB at a concentration of 3×10^{-5} mol/L give a very good fit between the values from modelling and experiments.

It is concluded that the trajectory model, based on surface chemistry and hydrodynamics, is able to explain the flotation results obtained from clay suspensions treated with HTAB. Although the results obtained from the model showed efficiency values about 15% higher than those obtained from experiments, the model also described a reduction of efficiency values at high recycle ratios due to floc breakage for Wyoming bentonite suspensions treated with HTAB.



Figure 9.28 Experimental results obtained from Wyoming bentonite suspensions treated with HTAB at a concentration of 1×10^{-5} mol/L, compared to results obtained from the trajectory model.



Figure 9.29 Experimental results obtained from Wyoming bentonite suspensions treated with HTAB at a concentration of 3 x 10^{-5} mol/L, compared to results obtained from the trajectory model.

9.4.2 Mixing zone model

The mixing zone model, proposed by Matsui and co-workers [93, 94] using a population balance, is shown in equations (4.42) and (4.44) as:

$$\frac{\mathrm{d}N_p}{\mathrm{d}t} = -k_1 N_p N_b \eta_a \tag{4.42}$$

$$k_T = a_1 \sqrt{\frac{p_{in}}{\mu V}} (d_b + d_p)^3$$
 (4.44)

where a_1 is the coefficient. For good mixing in the contact zone, the collision rate will be controlled by turbulent motion $(k_1 = k_T)$.

Following Tambo and Hozumi [133, 134], who presented flocculation kinetics as a function of grown-flocs and micro-flocs per unit volume per unit time, the coefficient may be modified to be a function of the mean collision-agglomeration factor between flocs and bubbles, \overline{P} , as given in equation (9.1).

$$a_1 \qquad = \qquad \frac{\pi}{6} \frac{9}{\sqrt{15}} \overline{P} \tag{9.1}$$

Tambo and co-workers also found that the mean collision-agglomeration factor value for a turbulent flocculator from their experiments was in the range of 0.019-0.027 and this factor was claimed to be dependent on the turbulent flow patterns [134].

Thus, the final equation can be written as:

$$\frac{\mathrm{d}N_p}{\mathrm{d}t} = -0.05 \sqrt{\frac{P_{in}}{\mu V}} V_f \eta_a N_p \qquad (9.2)$$

or

$$\frac{dN_{p}}{dt} = -0.026 \sqrt{\frac{P_{in}}{\mu V}} (d_{b} + d_{p})^{3} \eta_{a} N_{b} N_{p}$$
(9.3)

where V_f is the volumetric concentration of the aggregates introduced as $V_f = \frac{\pi}{6} N_b (d_b + d_p)^3$ and the value of 0.05 is the constant obtained from the average value of the mean collision-agglomeration factor multiplied by $(9/\sqrt{15})$. It can be seen that the coefficient is different from that originally used by Matsui and coworkers in their flotation model $(a_1 = 0.209)$.

An attachment efficiency, η_a , can be calculated from equation (4.23)

$$\eta_a = \exp\left(-\frac{E_1}{E_k}\right) \tag{4.23}$$

where E_1 is the energy barrier. E_k is the kinetic energy of the particles, described by Yoon and Mao [74], and given in equation (9.4)

$$E_{k} = \frac{2\pi r_{p}(\rho_{p} - \rho_{m})}{3}u_{rp}^{2}$$
(9.4)

where ρ_p is the particle density, ρ_m is the liquid density and u_{rp} is the particle velocity relative to that of a bubble.

When equations (4.23) and (9.4) were applied to the present case the attachment efficiency was found to be negligibly small. From the experimental data this cannot be correct. It is considered that the kinetic energy term as given by equation (9.4) is

not applicable in the present case. The reason is not fully understood but it seems that this energy equation can be applied accurately to spherical particles [74]. Clay particles normally form flocs with irregular shapes and sizes, and a lower density than the raw materials. From Table 9.1 the average separation distance at the energy barrier is about 20 nm, which differs from particle or floc diameters by about three orders of magnitude. Parts of the agglomerate surface may protrude beyond this separation distance to cause attachment. With such small separation distances simple smooth sphere models must become severely limited. The surface roughness may also create non uniform surface forces which can induce bubbles to attach to floc surfaces due to hydrodynamic, gravity and inertia forces. This indicates that it is difficult to apply the kinetic energy equation in the present work.

An alternative approach to calculate the attachment efficiency may be to consider another surface force instead of the kinetic energy. The maximum free energy per unit area at equilibrium, W_{132} , for material (1) attaching to material (2) in medium (3) is given by equation (9.5).

$$W_{132} = \gamma_{LV} (1 - \cos\theta) \tag{9.5}$$

where γ_{LV} is the surface tension of the water-air interface in this case and θ is the contact angle measured using water.

The free energy can be obtained by multiplying W_{132} by a contactable surface area, S_c , [75]. The contactable surface area is the area of molecules attaching to each other at the interface. For HTAB molecules Chen and co-workers found that the contactable surface area was 6.5 nm² [128]. Then the proposed attachment efficiency can be described by equation (9.6) solely in terms of surface energies. The kinetic and hydrodynamic energies for both bubble and particle are then included only in the turbulent motion term in Matsui and co-workers' model.

$$\eta_a = \exp\left(-\frac{E_1}{S_c W_{132}}\right) \tag{9.6}$$

Table 9.2 shows the energy barriers obtained from section 9.3, the free energy $S_c W_{132}$, and the attachment efficiencies for clay suspensions treated with HTAB in the concentration range of 1 x 10⁻⁶ to 5 x 10⁻⁵ mol/L. The free energy calculation is described in more detail in Appendix E7.

Table 9.2Attachment efficiencies of kaolin and Wyoming bentonite suspensionstreated with HTAB at various concentrations based on the proposed model.

Clay	HTAB concentration	Energy barrier, E_1	$S_c W_{132}$	η _{<i>a</i>}
	(mol/L)	(J)	(J)	(-)
kaolin	1 x 10 ⁻⁶	4.83 x 10 ⁻¹⁹	1.12×10^{-18}	0.65
	5 x 10 ⁻⁶	4.51 x 10 ⁻¹⁹	1.24 x 10 ⁻¹⁸	0.69
	1 x 10 ⁻⁵	4.26 x 10 ⁻¹⁹	1.37 x 10 ⁻¹⁸	0.73
	2×10^{-5}	3.64 x 10 ⁻¹⁹	1.46 x 10 ⁻¹⁸	0.78
	3 x 10 ⁻⁵	3.76 x 10 ⁻¹⁹	1.52×10^{-18}	0.78
bentonite	1 x 10 ⁻⁶	4.47 x 10 ⁻¹⁹	7.55 x 10 ⁻¹⁹	0.55
	5 x 10 ⁻⁶	5.15 x 10 ⁻¹⁹	1.42 x 10 ⁻¹⁸	0.69
	1 x 10 ⁻⁵	7.07 x 10 ⁻¹⁹	$1.45 \ge 10^{-18}$	0.61
	2×10^{-5}	9.03 x 10 ⁻¹⁹	$1.68 \ge 10^{-18}$	0.58
	3 x 10 ⁻⁵	$1.10 \ge 10^{-18}$	1.81×10^{-18}	0.54
	5×10^{-5}	1.52×10^{-18}	1.82×10^{-18}	0.43

These attachment efficiency values agree with Yoon and Mao [74] who claimed that attachment efficiencies were in the range of 0.45 to 0.93 and their values increased with increasing surfactant concentrations. These figures were also supported by

Edzwald [49] and Matsui and co-workers [93-95] who assumed attachment efficiencies of 0.5 and 0.4 respectively.

Table 9.2 shows that the attachment efficiency values for kaolin suspensions treated with HTAB increased with increasing HTAB concentrations. It is considered that the hydrophobic force is the controlling parameter [74] in this case. On the other hand, for Wyoming bentonite suspensions treated with HTAB, it can be seen that the attachment efficiency shows a maximum value at HTAB concentration of 5 x 10⁻⁶ mol/L. At low concentrations of HTAB the hydrophobic force is still the controlling parameter but as the concentration is increased the repulsive van der Waals force becomes dominant and η_a decreases.

In the trajectory model, a particle capture efficiency, η_{Tc} , is calculated directly from a consideration of all the forces involved. This could, however, be considered as the product of a collision efficiency, η_c , and an attachment efficiency. When floc sizes are slightly changed with increasing HTAB concentrations such as in the case of a kaolin suspension treated with HTAB, the above findings, when compared with experimental data, indicate that the collision efficiency is nearly constant. Then the attachment efficiency appears to be increased with increasing HTAB concentrations. For Wyoming bentonite treated with HTAB, it is difficult to conclude that the attachment efficiency is increased with further HTAB additions because floc sizes change when HTAB concentrations are increased.

When the attachment efficiencies are substituted in equation (9.3) as well as with other parameters, the flotation efficiencies give higher values than those obtained from experiments for both clay suspensions treated with HTAB. This result is not fully understood but it may be because the turbulent flow patterns between a flotation column and mixing tank and material types are different. Another contributory reason may be floc breakage in the pipework before the suspension reaches the column. Thus, the mean collision-agglomeration factor value estimated from equation (9.3), developed from mixing tank tests giving $a_1 = 0.026$, appears to be too high for flocbubble aggregates. The proposed model will use the result obtained from flotation tests to estimate the mean collision-agglomeration factor values using equation (9.1). The results are shown in Figures 9.30 to 9.33.

For a kaolin suspension treated with HTAB, the results obtained from modelling show that the coefficient values (a_1) are in the range 0.003-0.009 or the mean collision-agglomeration factor values are in the range of 0.0025-0.0074. The average value is about one order magnitude less than the values obtained from Tambo and co-workers' results as described in the previous section. The reason is that the coefficient for floc-bubble aggregates may be different from particle-particle aggregates. It can be seen that the coefficient values are increased with increasing HTAB concentrations. This indicates that the detachment efficiency may be increased with further HTAB additions.



Figure 9.30 Experimental results obtained from kaolin suspensions treated with HTAB at a concentration of 1 x 10^{-6} mol/L, compared to results obtained from flotation models (PT-model is the particle trajectory model and MZ-model is the mixing zone model: $a_1 = 0.0030$).



Figure 9.31 Experimental results obtained from kaolin suspensions treated with HTAB at a concentration of 5 x 10^{-6} mol/L, compared to results obtained from flotation models (PT-model is the particle trajectory model and MZ-model is the mixing zone model: $a_1 = 0.0045$).



Figure 9.32 Experimental results obtained from kaolin suspensions treated with HTAB at a concentration of 1 x 10^{-5} mol/L, compared to results obtained from flotation models (PT-model is the particle trajectory model and MZ-model is the mixing zone model: $a_1 = 0.0076$).



Figure 9.33 Experimental results obtained from kaolin suspensions treated with HTAB at a concentration of 2 x 10^{-5} mol/L, compared to results obtained from flotation models (PT-model is the particle trajectory model and MZ-model is the mixing zone model: $a_1 = 0.0086$).

For Wyoming bentonite suspensions treated with HTAB, however, the results obtained from the mixing zone model appear to describe the experimental results well at HTAB concentrations of 1×10^{-6} and 3×10^{-5} mol/L as shown in Figures 9.34 and 9.37 but it is not possible to fit the flotation results when floc sizes are decreased at high shear gradients shown in Figures 9.35 and 9.36. This result may indicate that particle or floc size changes have little effect on the model. Although the mixing zone model is unable to predict the results obtained from Wyoming bentonite treated with HTAB at concentrations of 5×10^{-6} and 1×10^{-5} mol/L, it is sufficiently promising to merit further development.



Figure 9.34 Experimental results obtained from Wyoming bentonite suspensions treated with HTAB at a concentration of 1 x 10^{-6} mol/L, compared to results obtained from flotation models (PT-model is the particle trajectory model and MZ-model is the mixing zone model: $a_1 = 0.0020$).



Figure 9.35 Experimental results obtained from Wyoming bentonite suspensions treated with HTAB at a concentration of 5 x 10^{-6} mol/L, compared to results obtained from flotation models (PT-model is the particle trajectory model and MZ-model is the mixing zone model: $a_1 = 0.0050$).



Figure 9.36 Experimental results obtained from Wyoming bentonite suspensions treated with HTAB at a concentration of 1 x 10^{-5} mol/L, compared to results obtained from flotation models (PT-model is the particle trajectory model and MZ-model is the mixing zone model: $a_1 = 0.0090$).



Figure 9.37 Experimental results obtained from Wyoming bentonite suspensions treated with HTAB at a concentration of 3 x 10^{-5} mol/L, compared to results obtained from flotation models (PT-model is the particle trajectory model and MZ-model is the mixing zone model: $a_1 = 0.0060$).
Figure 9.38 shows the effects of HTAB additions on the coefficient and attachment efficiency for both clay suspensions. It appears that both coefficient values and attachment efficiencies for kaolin suspensions treated with HTAB have increasing values with further HTAB concentration additions. However, at high concentrations, it appears that values are constant but they are likely to decrease with increasing HTAB concentration due to the decrease of contact angles using water. This implies that the optimum results for kaolin suspensions treated with HTAB may be found in the concentration range of 2×10^{-5} to 5×10^{-5} mol/L. Another contributory reason is that the repulsive electrostatic force is likely to be increased with increasing HTAB concentrations, while the hydrophobic force is decreased. For Wyoming bentonite suspensions treated with HTAB, the attachment efficiency is decreased when particle sizes are increased. This result was supported by Dai and co-workers [135].



Figure 9.38 Effects of HTAB additions on coefficient values and attachment efficiencies (KL is the kaolin, WB is the Wyoming bentonite, eff.con. is the coefficient and att.eff. is the attachment efficiency).

9.5 Summary

Flotation models can be used to describe flotation results obtained from the semicontinuous flotation rig. The trajectory model showed an increase in flotation efficiencies with increasing recycle ratios when suspensions treated with HTAB did not form flocs. For suspensions forming flocs with HTAB, the flotation efficiency results gave a maximum value at about 10% recycle ratio, which gave good agreement with the trajectory model. The models indicated also that particle or floc sizes, hydrodynamic behaviour and interfacial forces are the controlling factors for the flotation processes. A mixing zone model showed good results for only kaolin suspensions treated with HTAB. Finally, attachment efficiencies were increased with HTAB concentrations in the case of suspensions that did not form flocs, while their values were decreased with increasing floc sizes.

The trajectory model showed the better agreement with the experimental results in comparison to the mixing zone model. Thus it would be interesting to apply the trajectory model in a real water treatment plant.

Chapter 10

Conclusions

This work used two types of clay, kaolin and Wyoming bentonite, as representative raw materials because they are commonly found in natural waters. Three types of coagulant, alum, ferric chloride and polyaluminium chloride (PAC), and a cationic surfactant, hexadecyltrimethylammonium bromide (HTAB), were used for coagulation tests. Flotation trials were conducted at a range of concentrations of each coagulant and HTAB to seek an optimum result.

Floc characteristics, surface chemistry and the hydrodynamic forces between particles and bubbles are the important parameters underlying the mechanisms of flocculation and flotation processes. To study surface forces, zeta potentials and contact angle measurements were made on suspensions treated with coagulants and surfactants. Floc size distributions and floc strengths were also measured on similar suspensions. Finally, two flotation models, particle trajectory and mixing zone models, were proposed and they showed good agreement with experimental results, especially so for the trajectory model.

Gas bubbles were shown to be negatively charged in distilled water and this negative charge was changed to positive in cationic surfactant solutions. The positive charge increases with a rise in surfactant concentrations. The experimental results showed the points of zero charge to be at concentrations of 1.61 x 10^{-9} mol/L for HTAB, 1.69 x 10^{-8} mol/L for TTAB and 2.37 x 10^{-7} mol/L for DTAB, respectively. The zeta potentials of both clays also gave negative charges in tap water and dilute surfactant solutions. In HTAB solutions, the points of zero charge were at about 1.8 x 10^{-4} mol/L for kaolin particles and 2.9 x 10^{-5} mol/L for Wyoming bentonite particles. The points of zero charge were also obtained at about 50 mg/L for alum and ferric

chloride, and about 10 mg/L for PAC solutions with kaolin suspensions while, in Wyoming bentonite suspensions, those values were about 100 mg/L for alum and ferric chloride and about 35 mg/L for PAC solutions.

Interfacial forces are an important factor in attachment mechanisms in flotation. Both van der Waals and hydrophobic parameters can be obtained from contact angle measurements. The free energies showed that flocculation and flotation were possible when Wyoming bentonite suspensions were treated with HTAB. For kaolin suspensions, only high concentrations of HTAB solutions, above 2×10^{-5} mol/L, were predicted to give flocculation but flotation actually occurred in both cases with and without chemical additions.

Flocculation was tested at clay concentrations of 50 mg/L and 100 mg/L by treatment with alum and ferric chloride in the concentration range of 0-200 mg/L, and PAC concentrations up to 150 mg/L. Alum at 40 mg/L, ferric chloride at 40 mg/L and PAC at 10 mg/L were the selected coagulant dosages to be used in flotation tests. For the clay-HTAB-coagulant system, a HTAB concentration of 1×10^{-5} mol/L showed the optimum effect on flocculation efficiencies and this concentration was also used in the flotation tests. The hydrophobic forces were increased with increasing HTAB concentrations while hydration effects occurred upon the addition of coagulants to the suspensions. A flocculation model using the extended-DLVO theory produced good agreement with the experimental results.

The particle size measurements were performed using the off-line Lasentec apparatus while the effect of shear gradients on floc sizes was determined using the Lasentec apparatus fitted on-line in a mixing tank. These size distribution results were also used in explaining the results of the flocculation and flotation tests.

The results obtained from flotation tests for the clay suspensions treated with chemicals in this work were considered in two categories. Firstly, when particles

formed flocs, the optimum efficiency was at a recycle ratio of about 10%. At higher recycle ratios than 10%, the flotation efficiency values were decreased because flocs were broken by an increase of shear gradients. Secondly, when particles did not form flocs, the flotation efficiencies were increased with increasing the recycle ratios. An addition of small amounts of surfactants can produce hydrophobic forces. Experimental results showed that an increase in the hydrophobic forces was able to improve flotation efficiencies significantly.

Four proposed mechanisms of bubble-particle agglomerates for the clay suspensions treated with chemicals were introduced based on photographs taken inside a flotation column. HTAB molecules are adsorbed on bubble surfaces with the hydrocarbon tails inside the bubble volume while negatively charged particles are attached to ammonium groups under an electrostatic force.

The trajectory model gave good agreement with results obtained from the semicontinuous flotation rig. The model showed an increase in flotation efficiencies with increasing recycle ratios when suspensions treated with HTAB did not form flocs. For suspensions forming flocs with HTAB and the particle size affected by shear gradient, such as Wyoming bentonite treated with HTAB at concentrations of 5×10^{-6} mol/L, the flotation efficiency results gave maximum values at about 10% recycle ratio. The decreases of flotation efficiency at high recycle ratios is due to floc breakage. The model indicated that particle or floc sizes, hydrodynamic behaviour and interfacial forces are controlling factors in flotation processes. The mixing zone model was able to explain the results obtained from kaolin suspensions treated with HTAB but it was unable to predict the results from Wyoming bentonite. However, it is interesting enough to merit further development.

An understanding of flotation mechanisms is a key step in attempts to improve flotation efficiency. Flotation is a complicated interaction between the three phases in the process and some controlling parameters have been identified in this work. An

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increase in floc sizes produced good particle removal. Gentle feeding of the suspension into the flotation column is required to maintain low shear gradients in order to maintain floc sizes and flotation efficiencies. This study also showed that an increase in hydrophobic forces increased efficiencies due to more favourable interactions between bubbles and hydrophobic flocs. This suggests that small surfactant additions may give good results in real water treatment. Moreover, in theoretical study, it would be interesting to apply the trajectory model to a real water treatment plant.

Chapter 11

Suggestions for future work

To recalculate the number of HTAB molecules adsorbed on a bubble surface at equilibrium. Surface tension measurements for diluted surfactant solutions are required.

To improve the understanding of the flocculation mechanism of clay suspensions treated with coagulants, such as alum, surface energy measurements of $Al(OH)_{3(s)}$ and $Fe(OH)_{3(s)}$ may be required for a recalculation of ΔG_{132}^{TOT} where (1) = clay, (2) = $Al(OH)_{3(s)}$ or $Fe(OH)_{3(s)}$ and (3) = water.

Although contact angle measurements give reasonably accurate estimates of surface forces, direct force measurements such as via an atomic force microscope (AFM) are probably better. In recent years, many researchers have investigated hydrophobic interactions between dissimilar surfaces treated with surfactant solutions in this way but kaolin and Wyoming bentonite surfaces have not been subject to such tests.

Clearly, hydrophobic interaction is a substantial parameter in flotation and this force is normally controlled using long chain organic compounds such as surfactants. Alkyl-ammonium bromide has produced significant results in the removal of clay suspensions. However, alternative chemicals such as secondary or tertiary organic compounds should be investigated.

A high speed camera will be required to study the attachment mechanism inside a flotation column. Using a photo technique, the number of bubbles attached to flocs may be studied along the column, which will provide information to improve the

understanding of the flotation mechanism, the attachment and detachment of bubbles from flocs.

The effects of surfactants on bubble size distribution and number of bubbles introduced into a column are required to provide more information to describe the flotation results obtained from suspensions treated with the surfactants.

Although clays are commonly used as representative raw materials in water treatment processes, the complicated surfaces and structures of clay flocs are more difficult to describe especially in the interaction between bubble and floc surfaces. To understand better the effects of surface forces, synthesised particles such as latex and glass beads should be used to investigate the interaction between particles and bubbles.

The mixing zone length is one of the important parameters in calculating the energy dissipation during the injection of liquid streams into a flotation column. An experimental study is required of the injection of liquid streams into free space and into a column.

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Appendix A

Properties of substances

Table A1. Relationship between temperature, viscosity and permittivity of water at 1 atm [136].

Temp.	viscosity	permittivity	Temp.	viscosity	permittivity
(°C)	x 10 ⁴ (Pa-S)	x 10 ¹⁰ (F/m)	(°C)	x 10 ⁴ (Pa-S)	x 10 ¹⁰ (F/m)
25	8.711	6.937	38	6.620	6.539
26	8.520	6.906	39	6.493	6.508
27	8.328	6.875	40	6.367	6.478
28	8.137	6.844	41	6.311	6.449
29	7.945	6.813	42	6.255	6.420
30	7.754	6.782	43	6.199	6.390
31	7.603	6.752	44	6.143	6.361
32	7.452	6.721	45	5.807	6.332
33	7.301	6.691	46	5.712	6.303
34	7.150	6.660	47	5.617	6.274
35	6.999	6.630	48	5.523	6.245
36	6.873	6.600	49	5.428	6.216
37	6.746	6.569	50	5.333	6.187

Table A2. Relationship between temperature and apparatus (Rank Brothers)temperature scale.

Temp. ^o C	25	30	35	40	45	50
Scale	620	765	780	835	880	920

Appendix B

Tap water analysis

Water from the town's water taps in the Department of Chemical Engineering, Loughborough University, was used to prepare clay suspensions for both laboratory and pilot tests. The water analysis in this section was performed using a titration technique for alkalinity measurement [137] and ion chromatography for the concentration of basic cations.

B.1 Alkalinity

B.1.1 Reagents

Standard hydrochloric acid 0.02N

Stock acid solution was prepared by diluting 8.3 ml conc HCl to 1 litre with distilled water. Then, the 0.02*N* hydrochloric acid was prepared by diluting 200 ml of the 0.1*N* stock solution to 1 litre with deionised water treated to give a conductance less than 2 $\mu\Omega$ /cm. The 0.02*N* hydrochloric acid was standardised against a 0.020*N* sodium bicarbonate solution which had been prepared by dissolving 1.060 gram anhydrous Na₂CO₃ (primary grade), dried at 140°C overnight, to 1 litre with deionised water. The standardisation was performed as a typical alkalinity titration by using phenolphthalein indicator for phenolphthalein alkalinity and methyl orange indicator for total alkalinity.

B.1.2 Procedure

50 ml of sample was dosed with 4-drops of phenolphthalein indicator. If sample colour is pink, the phenolphthalein alkalinity will be performed by titrating with

0.02N standard hydrochloric acid. If sample colour is white, it means no carbonate alkalinity in a sample. After the phenolphthalein alkalinity had been determined, the solution was treated with 4-drops of methyl orange indicator and titrated against 0.02N standard hydrochloric acid until the sample colour was changed from white to orange.

B.1.3 Calculation

Phenolphthalein alkalinity =
$$\frac{A \times N \times 50,000}{\text{ml sample}}$$
 [mg/1 CaCO₃]
Total alkalinity = $\frac{B \times N \times 50,000}{\text{ml sample}}$ [mg/1 CaCO₃]

where A is the volume (ml) of acid required to reach the phenolphthalein end point, B is the volume (ml) to reach the second end point and N is the normality of standard acid.

Three types of alkalinity are defined namely, carbonate, hydroxide and bicarbonate alkalinity. Carbonate alkalinity is represented when the phenolphthalein alkalinity is not zero but it is less than the total alkalinity. Hydroxide alkalinity is represented when the phenolphthalein alkalinity is more than half the total alkalinity and bicarbonate alkalinity is represented when the phenolphthalein is represented when the phenolphthalein alkalinity is less than half the total alkalinity is less than half the total alkalinity.

B.2 Ion chromatography

A Dionex series 4500I ion chromatography with an ionpac CS12 analytical column was used to determine the concentration of cations namely, Na^+ , K^+ , Mg^{2+} and Ca^{2+} . This method is similar in operation to high performance liquid chromatography, HPLC. After the sample is injected, the mobile phase will transfer it through the

analytical column separating ions by ion affinity. The elution sequence of separated ions is detected using the conductivity detector, UV/VIS or fluorescence detector [138].

In comparison to the results obtained from Severn Trent Water for town's water, the tap water used in our experiments gave lower alkalinity and ion concentrations as shown in Table B1. The total alkalinity result also indicated only bicarbonate alkalinity because the phenolphthalein alkalinity was not found in our samples.

Parameters	Tap water from pilot plant	Town tap-water
ave. temperature (° C)	15-19	10.2
Sodium ion (mg/L)	24	37
Potassium ion (mg/L)	2.8	5.2
Magnesium ion (mg/L)	10	15
Calcium ion (mg/L)	49	90
рН	7.1	. 7.6
Total hardness (mg/L)	162	287
Alkalinity (mg/L)	122	153

Table B1 Comparison between sample and town tap water (Severn Trent Water)

Appendix C

Experimental data

Table C1	Electromobilities of	f bubbles in DT/	AB solutions treated	with 1 mg/L of NaCL
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DTAB conc.	DTAB conc.	electromobilities	S.D	pН	ave. bubble
(mg/L)	(mol/L)	(µms ⁻¹ /Vcm ⁻¹)			size (µm)
distilled water	0	-1.420	0.50	5.63	27
0.015	4.86E-08	-1.070	0.45	6.15	29
0.03	9.73E-08	-0.655	0.26	6.15	30
0.1	3.24E-07	0.445	0.17	5.61	27
0.5	1.62E-06	1.326	0.37	5.65	27
1.0	3.24E-06	1.563	0.48	5.78	26

Table C2 Electromobilities of bubbles in DTAB solutions.

DTAB conc.	DTAB conc.	electromobilities	S.D	pН	ave. bubble
(mg/L)	(mol/L)	(µms ⁻¹ /Vcm ⁻¹)			size (µm)
1	3.24E-06	1.994	0.65	6.56	30
3	9.73E-06	1.953	0.72	6.30	26
6	1.95E-05	2.257	0.82	6.21	29
12.5	4.05E-05	2.890	0.75	5.62	27
75	2.43E-04	3.311	0.81	5.90	24
150	4.86E-04	5.227	1.26	5.29	25
175	5.68E-04	5.359	0.85	5.65	29
200	6.49E-04	6.012	1.08	5.80	29
300	9.73E-04	7.079	1.23	5.96	30
610	1.98E-03	7.249	1.13	5.96	25
1524	4.94E-03	8.332	1.20	5.77	26
3048	9.89E-03	7.568	1.60	5.17	25

TTAB conc.	TTAB conc.	electromobilities	S.D	pН	ave. bubble
(mg/L)	(mol/L)	$(\mu m s^{-1}/V cm^{-1})$			size (µm)
distilled water	0	-1.420	0.50	5.63	27
0.001	2.97E-09	-0.771	0.32	5.31	28
0.002	5.94E-09	-0.503	0.40	6.27	27
0.004	1.19E-08	-0.408	0.27	5.85	28
0.005	1.49E-08	-0.422	0.20	5.76	28
0.006	1.78E-08	0.314	0.20	6.15	26
0.008	2.38E-08	0.441	0.23	5.92	25
0.01	2.97E-08	0.701	0.33	5.24	29
0.02	5.94E-08	0.643	0.30	5.98	25
0.05	1.49E-07	0.648	0.30	6.28	28
0.1	2.97E-07	1.080	0.32	6.27	32
0.5	1.49E-06	1.338	0.39	5.80	28
1.0	2.97E-06	2.458	0.67	5.16	26

Table C3 Electromobilities of bubbles in TTAB solutions in the presence of 1 mg/L of NaCl.

Table C4 Electromobilities of bubbles in TTAB solutions.

TTAB conc.	TTAB conc.	electromobilities	S.D	pН	ave. bubble
(mg/L)	(mol/L)	(µms ⁻¹ /Vcm ⁻¹)			size (µm)
8	2.38E-05	1.871	0.65	5.91	27
16	4.76E-05	3.094	0.55	5.69	24
24	7.13E-05	2.338	0.75	5.78	29
32	9.51E-05	2.814	0.54	5.86	26
40	1.19E-04	3.040	0.69	5.45	28
60	1.78E-04	3.032	0.66	5.61	26
80	2.38E-04	3.390	1.03	5.62	27
100	2.97E-04	4.918	1.08	5.05	27
168.2	5.00E-04	5.199	1.60	5.10	27
336.4	1.00E-03	6.056	1.77	5.78	29

HTAB conc.	HTAB conc.	electromobilities	S.D	pH	ave. bubble
(mg/L)	(mol/L)	(µms ⁻¹ /Vcm ⁻¹)			size (µm)
distilled water	0	-1.420	0.50	5.63	27
0.0001	2.74E-10	-1.370	0.53	5.66	27
0.0002	5.48E-10	-0.538	0.29	5.63	26
0.0004	1.10E-09	-0.525	0.30	5.69	26
0.0005	1.37E-09	-0.709	0.33	5.60	27
0.0006	1.65E-09	0.423	0.26	5.45	27
0.0008	2.19E-09	0.752	0.31	5.45	29
0.001	2.74E-09	0.790	0.26	5.64	24
0.005	1.37E-08	0.878	0.48	5.47	30
0.01	2.74E-08	0.892	0.29	5.42	30
0.05	1.37E-07	0.905	0.33	5.50	26
0.1	2.74E-07	1.245	0.30	5.46	28
0.5	1.37E-06	2.338	1.14	5.63	23

Table C5 Electromobilities of bubbles in HTAB solutions treated with 1 mg/L of NaCl.

Table C6 Electromobilities of bubbles in HTAB solutions.

HTAB conc.	HTAB conc.	electromobilities	S.D	pН	ave. bubble
(mg/L)	(mol/L)	(µms ⁻¹ /Vcm ⁻¹)			size (µm)
0.5	1.37E-06	2.432	0.60	5.62	28
1	2.74E-06	2.416	0.95	5.35	30
3	8.23E-06	2.354	0.58	5.67	29
4	1.10E-05	2.510	0.56	5.63	24
6	1.65E-05	2,759	0.67	5.61	35
12	3.29E-05	3.235	0.59	5.85	25
20	5.49E-05	3.757	0.74	5.45	26
30	8.23E-05	3.741	1.10	5.26	29

HTAB (mol/L)	water	Glycerol	DIM	BNL
0	31.8	29.3	27.6	23.0
1.00E-06	50.4	54.3	39.4	31.9
5.00E-06	53.4	56.7	45.4	36.5
1.00E-05	56.2	59.3	47.2	42.0
2.00E-05	58.2	60.2	49.8	44.8
3.00E-05	59.5	60.0	50.2	44.8
5.00E-05	61.8	58.4	55.2	46.0

Table C7 Average contact angles of kaolin-HTAB surfaces.

Table C8 Average contact angles of kaolin-coagulant surfaces.

Coagulants (mg/L)	water	Glycerol	DIM	BNL
Alum (40)	30.9	34.4	36.3	20.0
Alum (50)	31.4	32.2	36.5	21.7
Alum (60)	29.1	31.2	37.0	24.5
FeCl ₃ (40)	30.5	40.4	33.7	27.1
FeCl ₃ (50)	27.0	35.4	32.2	24.8
FeCl ₃ (60)	26.1	33.7	32.0	19.6
PAC (10)	44.1	49.6	36.4	26.4
PAC (15)	40.2	46.1	33.5	23.1
PAC (20)	32.3	42.2	32.2	18.9

Table C9 Average contact angles of kaolin-HTAB-coagulant surfaces.

Coagulants (mg/L)	water	Glycerol	DIM	BNL
Alum (40)	49.7	47.5	35.9	32.0
FeCl ₃ (40)	53.9	55.1	37.0	28.7
PAC (10)	49.9	51.8	36.9	29.8

HTAB concentration is 1×10^{-5} mol/L

HTAB	water	Glycerol	DIM	BNL
0	22.2	20.7	26.1	21.7
1.00E-06	41.0	46.0	39.0	30.0
5.00E-06	57.3	55.6	40.6	39.0
1.00E-05	58.0	55.6	42.2	41.0
2.00E-05	63.0	55.8	44.1	43.2
3.00E-05	65.7	59.0	45.6	41.8
5.00E-05	65.8	59.2	48.3	42.0

Table C10	Average c	ontact an	gles of	Wyoming	bentonite-HTAB	surfaces.
			0			

Table C11 Average contact angles of Wyoming bentonite-coagulant surfaces.

Coagulants (mg/L)	water	Glycerol	DIM	BNL
Alum (40)	25.8	34.2	31.2	24.1
Alum (50)	29.3	35.5	27.7	25.2
Alum (60)	29.2	37.0	25.8	25.0
FeCl ₃ (40)	24.9	31.7	28.9	23.8
FeCl ₃ (50)	29.4	32.4	29.3	24.3
FeCl ₃ (60)	29.2	38.6	29.6	26.5
PAC (10)	23.6	30.2	26.4	23.8
PAC (15)	24.0	37.7	30.3	23.1
PAC (20)	27.0	40.0	31.2	22.5

Table C12 Average contact angles of Wyoming bentonite-HTAB-coagulant surfaces.

Coagulants (mg/L)	water	Glycerol	DIM	BNL
Alum (40)	52.6	53.1	33.1	29.9
FeCl ₃ (40)	54.1	54.8	36.7	29.3
PAC (10)	52.3	52.6	33.2	27.3

HTAB concentration is 1 x 10⁻⁵ mol/L

Chemicals	Agitator speed (rpm)					
	100	125	150	175	200	
HTAB (5 x 10 ⁻⁶ M)	13.9	-	13.7	-	13.1	
HTAB (1 x 10 ⁻⁵ M)	14.3	-	14.2	-	14.3	
HTAB (2 x 10 ⁻⁵ M)	15.6	-	15.2	-	15.0	
HTAB (5 x 10 ⁻⁵ M)	15.5	-	15.3	-	15.3	
alum (40mg/L)	37.3	-	29.6	-	21.0	
FeCl ₃ (40mg/L)	51.2	45.9	41.4	35.4	31.0	
PAC (10 mg/L)	32.5	24.7	22.3	18.3	17.2	
alum (40mg/L)*	31.8	-	21.4	-	18.5	
FeCl ₃ (40mg/L)*	41.1	-	34.8	-	27.1	
PAC (10 mg/L)*	31.5	-	21.7	-	17.1	

Table C13 Mean particle size of kaolin suspensions treated with HTAB and coagulants

treated with HTAB concentration at 1×10^{-5} mol/L.

Chemicals	Agitator speed (rpm)					
	100	125	150	175	200	250
HTAB (1 x 10 ⁻⁶ M)	12.7	-	11.8	-	11.9	-
HTAB (5 x 10 ⁻⁶ M)	17.1	12.4	12.0	11.5	10.5	-
HTAB (1 x 10 ⁻⁵ M)	32.2	26.3	23.4	19.6	16.3	12.5
HTAB (2 x 10 ⁻⁵ M)	65.1	-	59.4 .	-	47.8	39.0
HTAB (3 x 10 ⁻⁵ M)	80.3	-	77.2	-	70.3	63.1
HTAB (5 x 10 ⁻⁵ M)	88.5	-	84.0	-	80.7	73.4
alum (40mg/L)	10.8	-	10.6	-	10.7	-
FeCl ₃ (40mg/L)	14.8	12.8	11.8	-	11.6	-
PAC (10 mg/L)	12.3	-	11.7	-	11.8	11.6
alum (40mg/L)*	16.9	-	13.9	-	10.5	9.7
FeCl ₃ (40mg/L)*	23.7	-	16.9	-	12.7	•
PAC (10 mg/L)*	25.9	-	18.3	-	12.9	-

treated with HTAB concentration at 1×10^{-5} mol/L.

.

Coagulant conc. (mg/L)	initial pH	final pH	initial turbidity (ntu)	final turbidity (ntu)	efficiency (%)
0	7.3	7.3	30.5	30.5	0
5	7.3	7.1	29.5	15.8	46.6
10	7.3	7.1	29.5	5.3	82.2
15	7.3	7.0	29.5	3.7	87.6
20	7.3	7.0	29.5	2.5	91.7
30	7.3	6.9	29.5	1.5	94.9
40	7.3	6.8	29.5	1.2	95.9
50	7.3	6.5	31.5	0.5	98.6
60	7.3	6.4	31.5	0.5	98.6
80	7.3	6.3	31.5	0.6	98.3
100	7.3	6.2	31.5	0.6	98.3
150	7.3	5.8	31.5	1.3	96.0
200	7.3	5.5	31.5	1.1	96.5

Table C15 Jar tests for KL at a concentration of 50 mg/L treated with alum solutions.

Table C16 Jar tests for KL at a concentratio	n of 100 mg/L treated with alum solutions.
----------------------------------------------	--------------------------------------------

Coagulant	initial pH	final pH	initial turbidity	final turbidity	efficiency (%)
conc. (mg/L)			(ntu)	(ntu)	
0	7.3	7.3	62.5	63.5	0
5	7.3	7.2	62.5	15.5	75.2
10	7.3	7.1	62.5	7.5	88.1
- 15	7.3	7.0	62.5	6.2	90.1
20	7.3	7.0	62.5	4.7	92.5
30	7.3	6.9	62.5	2.2	96.5
40	7.3	6.8	62.5	2.0	96.8
50	7.3	6.4	64.5	1.8	97.2
60	7.3	6.4	64.5	1.0	98.4
80 ·	7.3	6.2	64.5	0.7	98.9
100	7.3	6.1	64.5	0.9	98.7
150	7.3	5.8	64.5	1.1	98.3
200	7.3	5.4	64.5	1.4	97.9

Coagulant conc. (mg/L)	initial pH	final pH	initial turbidity (ntu)	final turbidity (ntu)	efficiency (%)
0	7.4	7.4	31.5	31.5	0
5	7.4	7.1	31.5	5.4	82.6
10	7.4	7.0	31.5	3.2	89.8
15	7.4	6.9	31.5	2.5	91.9
20	7.4	6.8	31.5	1.9	93.8
30	7.4	6.6	31.5	2.1	93.2
40	7.4	6.5	31.5	2.1	93.3
50	7.3	6.1	31.5	1.1	96.3
60	7.3	6.0	31.5	1.1	96.5
80	7.3	5.8	31.5	1.2	96.0
100	7.3	5.4	31.5	1.6	94.9
150	7.3	3.5	31.5	3.0	90.3
200	7.3	2.8	31.5	21.0	33.3

Table C17 Jar tests for KL at a concentration of 50 mg/L treated with ferric chloride solutions.

Table C18 Jar tests for KL at a concentration of 100 mg/L treated with ferric chloride solutions.

Coagulant	initial pH	final pH	initial turbidity	final turbidity	efficiency (%)
conc. (mg/L)			(ntu)	(ntu)	
0	7.4	7.4	63.5	63.5	0
5	7.4	7.0	63.5	7.8	87.6
10	7.4	6.9	63.5	4.8	92.4
15	7.4	6.8	63.5	4.2	93.4
20	7.4	6.8	63.5	3.4	94.6
30	7.4	6.5	63.5	2.5	96.1
40	7.4	6.4	63.5	2.2	96.5
50	7.3	6.1	63.5	1.5	97.6
60	7.3	6.0	63.5	1.8	97.1
80	7.3	5.8	63.5	1.7	97.3
100	7.3	5.5	63.5	1.3	97.9
150	7.3	3.9	63.5	3.4	94.6
200	7.3	2.8	63.5	7.9	87.6

Coagulant	initial pH	final pH	initial turbidity	final turbidity	efficiency (%)
conc. (mg/L)			(ntu)	(ntu)	
0	7.3	7.3	32.5	32.5	0
0.5	7.3	7.2	33.0	24.0	27.3
1	7.3	7.2	33.0	13.5	59.1
2	7.3	7.1	33.0	3.9	88.2
3	7.3	7.0	32.0	2.6	92.0
5	7.3	6.9	32.0	1.1	96.6
10	7.3	6.7	32.0	0.5	98.6
15	7.3	6.6	32.0	0.2	99.4
20	7.3	6.4	32.0	0.2	99.4
30	7.3	6.2	32.0	0.5	98.6
40	7.3	5.9	33.0	0.6	98.3
60	7.3	5.6	33.0	0.4	98.8
80	7.3	4.8	33.0	0.6	98.3
	-				

Table C19 Jar tests for KL at a concentration of 50 mg/L treated with PAC solutions.

Table C20 Jar tests for KL at a concentration of 100 mg/L treated with PAC solutions.

Coagulant	initial pH	final pH	initial turbidity	final turbidity	efficiency (%)
conc. (mg/L)			(ntu)	(ntu)	
0	7.3	7.3	64.5	64.5	0
3	7.3	7.0	65.0	5.4	91.7
5	7.3	6.9	64.0	4.8	92.5
10	7.3	6.8	64.0	1.1	98.3
15	7.3	6.6	64.0	0.7	99.0
20	7.3	6.5	64.0	0.5	99.3
30	7.3	6.2	64.0	0.4	99.5
40	7.3	6.0	64.0	0.4	99.4
50	7.3	5.6	64.5	1.1	98.4
60	7.3	5.4	64.5	1.2	98.1
80	7.3	4.7	64.5	1.1	98.4
100	7.3	4.1	64.5	2.5	96.2
150	7.3	3.8	64.5	3.2	95.1

Coagulant	initial pH	final pH	initial turbidity	final turbidity	efficiency (%)
conc. (mg/L)			(ntu)	(ntu)	
0	7.4	7.4	10.0	10.0	0
1	7.4	7.4	10.0	2.7	73.5
2	7.4	7.4	10.0	2.2	78.0
3	7.4	7.3	10.0	1.9	81.5
5	7.2	7.1	11.0	0.2	97.7
10	7.2	7.0	11.0	0.1	98.6
15	7.2	6.9	11.0	0.1	98.6
20	7.2	6.8	11.0	0.1	98.6
30	7.2	6.6	11.0	0.2	98.1
40	7.2	6.5	11.0	0.1	98.6
50	7.4	6.5	10.0	0.5	95.0
60	7.4	6.5	10.0	0.6	94.0
80	7.4	6.3	10.0	0.8	92.0
100	7.4	6.2	10.0	0.8	92.0
150	7.4	5.9	10.0	1.1	89.5
200	7.4	5.5	10.0	1.2	87.5

Table C21 Jar tests for WB at a concentration of 50 mg/L treated with alum solutions.

Table C22 Jar tests for WB at a concentration of 100 mg/L treated with alum solutions.

Coagulant	initial pH	final pH	initial turbidity	final turbidity	efficiency (%)
conc. (mg/L)			(ntu)	(ntu)	
0	7.4	7.4	19.5	19.5	0
1	7.4	7.3	19.0	2.1	89.2
2	7.4	7.3	19.0	1.6	91.3
3	7.4	7.2	19.0	0.7	96.0
5	7.4	7.2	20.0	0.7	96.2
10	7.4	7.0	20.0	0.5	97.2
15	7.4	6.9	20.0	0.3	98.2
20	7.4	6.8	20.0	0.2	98.7
30	7.4	6.6	20.0	0.1	99.7
40	7.4	6.6	20.0	0.1	99.7
50	7.4	6.6	20.0	0.5	97.2
60	7.4	6.5	20.0	0.5	97.8
80	7.4	6.3	20.0	0.6	97.1
100	7.4	6.2	20.0	0.7	96.3
150	7.4	6.0	20.0	1.0	94.9
200	7.4	5.9	20.0	1.0	95.1

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Coagulant	initial pH	final pH	initial turbidity	final turbidity	efficiency (%)
conc. (mg/L)		- - -	(ntu)	(ntu)	
0	7.4	7.4	10.0	10.0	0
5	7.4	7.1	10.0	3.3	67.0
10	7.4	7.0	10.0	2.3	77.0
15	7.4	6.9	10.0	1.0	90.0
20	7.4	6.8	10.0	0.9	90.5
30	7.4	6.7	10.0	0.7	92.5
40	7.4	6.5	10.0	0.6	94.0
50	7.4	6.3	10.0	0.6	93.5
60	7.4	6.2	10.0	0.5	94.5
80	7.4	6.0	10.0	0.7	92.5
100	7.4	5.6	10.0 ·	0.6	94.0
150	7.4	4.1	10.0	0.9	90.5
200	7.4	2.9	10.0	3.2	67.5

Table C23 Jar tests for WB at a concentration of 50 mg/L treated with ferric chloride solutions.

Table C24 Jar tests for WB at a concentration of 100 mg/L treated with ferric chloride solutions.

Coagulant	initial pH	final pH	initial turbidity	final turbidity	efficiency (%)
conc. (mg/L)			(ntu)	(ntu)	
0	7.4	7.4	20.0	20.0	0
5	7.4	7.1	20.0	2.3	88.7
10	7.4	7.0	20.0	1.8	91.0
15	7.4	6.8	20.0	1.1	94.3
20	7.4	6.8	20.0	0.6	97.0
30	7.4	6.6	20.0	0.5	97.5
40	7.4	6.5	20.0	0.4	98.0
50	7.4	6.2	20.0	0.8	96.0
60	7.4	6.1	20.0	0.8	96.0
80	7.4	5.8	20.0	1.0	95.0
100	7.4	5.6	20.0	1.1	94.2
150	7.4	4.4	20.0	1.5	92.2
200	7.4	2.8	20.0	1.6	91.7

Coagulant conc. (mg/L)	initial pH	final pH	initial turbidity (ntu)	final turbidity (ntu)	efficiency (%)
0	7.4	7.4	10.0	10.0	0
1	7.4	7.3	10.0	1.9	81.0
2	7.4	7.2	10.0	0.9	90.5
3	7.4	7.1	10.0	0.6	94.0
5	7.4	6.9	10.0	0.7	92.5
10	7.4	6.6	10.0	0.5	94.5
15	7.4	6.5	10.0	0.2	97.5
20	7.4	6.4	10.0	0.3	97.0
30	7.4	6.2	10.0	1.1	89.0
40	7.4	5.9	10.0	2.2	77.5

Table C25 Jar tests for WB at a concentration of 50 mg/L treated with PAC solutions.

Table C26 Jar tests for WB at a concentration of 100 mg/L treated with PAC solutions.

Coagulant	initial pH	final pH	initial turbidity	final turbidity	efficiency (%)
conc. (mg/L)			(ntu)	(ntu) (ntu)	
0	7.4	7.4	20.0	20.0	0
0.2	7.4	7.3	20.0	4.0	80.5
0.5	7.4	7.3	20.0	1.4	92.7
1	7.4	7.3	21.0	0.8	96.2
2	7.4	7.2	21.0	0.4	97.8
3	7.4	7.2	21.0	0.5	97.4
5	7.4	6.9	21.0	0.5	97.4
10	7.4	6.7	21.0	0.4	97.8
15	7.4	6.5	21.0	0.5	97.4
20	7.4	6.4	21.0	0.5	97.5
30	7.4	6.2	21.0	0.4	97.8
40	7.4	6.0	21.0	0.6	97.1
50	7.4	5.6	20.0	0.6	97.0
60	7.4	5.4	20.0	0.4	97.9
80	7.4	4.8	20.0	0.4	97.9
100	7.4	4.2	20.0	2.0	90.1
150	7.4	4.0	20.0	14.5	26.6
200	7.4	3.8	20.0	29.0	

Coagulant	HTAB conc.	initial pH	final pH	initial turbidity	final turbidity	efficiency
type	(mol/L)			(ntu)	(ntu)	(%)
alum at	0	7.3	7.1	30.0	15.8	46.6
5 mg/L	1.0E-07	7.3	7.2	30.0	18.3	39.2
	1.0E-06	7.3	7.2	30.0	17.5	41.7
	1.0E-05	7.3	7.2	30.0	20.0	33.3
ferric	0	7.3	7.1	31.0	5.4	82.8
chloride	1.0E-07	7.3	7.2	28.0	4.7	83.4
at 5 mg/L	1.0E-06	7.3	7.2	28.0	4.5	83.9
	1.0E-05	7.3	7.2	28.0	5.0	82.3
PAC at	0	7.3	7.1	33.0	13.5	59.1
l mg/L	1.0E-07	7.3	7.2	29.0	12.3	57.7
	1.0E-06	7.3	7.2	29.0	14.0	51.7
	1.0E-05	7.3	7.2	29.0	16.0	44.8

Table C27 Jar tests for KL at a concentration of 50 mg/L treated with coagulants and HTAB solutions.

Table C28 Jar tests for KL at a concentration of 100 mg/L treated with coagulants and HTAB solutions.

Coagulant	HTAB conc.	initial pH	final pH	initial turbidity	final turbidity	efficiency
type	(mol/L)			(ntu)	(ntu)	(%)
alum at	0	7.3	7.2	63.0	15.5	75.2
5 mg/L	1.0E-07	7.3	7.2	65.0	17.5	73.1
	1.0E-06	7.3	7.2	65.0	17.0	73.8
	1.0E-05	7.3	7.2	65.0	17.5	73.1
ferric	0	7.4	7.0	63.0	7.9	87.6
chloride	1.0E-07	7.3	7.1	63.0	5.7	90.9
at 5 mg/L	1.0E-06	7.3	7.1	63.0	5.4	91.4
	1.0E-05	7.3	7.1	63.0	6.6	89.5
PAC at	1.0E-07	7.3	7.2	61.0	16.5	72.9
l mg/L	1.0E-06	7.3	7.2	61.0	17.0	72.1
	1.0E-05	7.3	7.2	61.0	18.0	70.5
Coagulant	HTAB conc.	initial pH	final pH	initial turbidity	final turbidity	efficiency
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type	(mol/L)			(ntu)	(ntu)	(%)
alum at	0	7.3	7.1	11.0	0.2	97.7
5 mg/L	1.0E-07	7.3	7.2	10.0	0.5	95.0
	1.0E-06	7.3	7.2	10.0	0.2	97.5
	1.0E-05	7.3	7.2	10.0	0.4	96.0
ferric	0	7.4	7.1	10.0	3.3	67.0
chloride	1.0E-07	7.3	7.1	10.0	3.6	63.5
at 5 mg/L	1.0E-06	7.3	7.1	10.0	2.0	80.0
	1.0E-05	7.3	7.1	10.0	0.6	93.5
PAC at	1.0E-07	7.3	7.2	10.0	2.3	77.3
0.5 mg/L	1.0E-06	7.3	7.2	10.0	2.5	75.3
	1.0E-05	7.3	7.2	10.0	0.4	96.3

Table C29 Jar tests for WB at a concentration of 50 mg/L treated with coagulants and HTAB solutions.

Table C30 Jar tests for WB at a concentration of 100 mg/L treated with coagulants and HTAB solutions.

Coagulant	HTAB conc.	initial pH	final pH	initial turbidity	final turbidity	efficiency
type	(mol/L)			(ntu)	(ntu)	(%)
alum at	0	7.4	7.1	20.0	1.9	90.5
5 mg/L	1.0E-07	7.4	7.2	20.0	1.3	93.3
	1.0E-06	7.4	7.2	20.0	1.4	92.9
	1.0E-05	7.4	7.2	20.0	0.6	97.0
ferric	0	7.4	6.5	20.0	0.4	9 7.7
chloride	1.0E-07	7.4	6.4	20.0	0.5	97.5
at 40	1.0E-06	7.4	6.4	20.0	0.3	98.2
mg/L	1.0E-05	7.4	6.4	20.0	0.5	97.2
ferric	0	7.4	7.1	20.0	2.0	89.8
chloride	1.0E-07	7.4	7.2	20.0	1.7	91.7
at 5 mg/L	1.0E-06	7.4	7.2	20.0	1.1	94.5
	1.0E-05	7.4	7.2	20.0	1.0	94.8
PAC at	0	7.4	7.2	20.0	2.8	86.0
0.5 mg/L	1.0E-07	7.4	7.4	20.0	1.5	92.3
	1.0E-06	7.4	7.4	20.0	1.1	94.3
	1.0E-05	7.4	7.4	20.0	0.9	95.3

Coagulant	mean chord lengths of clays with various coagulant treatments							
conc.								
(mg/L)	Alum(KL)	Ferric(KL)	PAC(KL)	Alum(WB)	Ferric(WB)	PAC(WB)		
0	16.43	18.46	18.09	7.025	7.92	7.92		
0.5	-	-	14.67		-	-		
1	-	-	20.98	11.14	-	8.12		
2	-	-	31.04	7.32		7.32		
3	-	-	45.19	8.00	-	8.78		
5	19.60	33.78	43.44	12.53	10.53	8.45		
10	23.98	30.53	44.31	-	8.025	12.30		
15	32.43	38.29	49.36	10.57	14.65	13.56		
20	35.67	61.41	51.43	10.91	15.51	12.32		
30	36.71	47.90	47.94	8.23	15.68	11.50		
40	47.91	44.47	49.58	6.69	18.50	10.76		
50	57.81	59.71	-	7.36	22.19	-		
60	52.97	59.65	41.37	6.92	15.67	-		
80	45.91	41.61	47.90	5.90	17.62	-		
100	45.14	63.30	-	5.73	-	-		
150	36.16	64.54	•	9.68	-	-		
200	32.80	62.43	-	8.39	-	-		

Table C31 Mean chord lengths of caly particles at a concentration of 50 mg/L treated with coagulants in flocculation tests.

Table C32	Mean chord lengths of caly particles at a concentration of 100 mg/L treated with
coagulants	in flocculation tests.

Coagulant	mean chord lengths of clays with various coagulant treatments					
conc.			. <u>.</u>			· •
(mg/L)	Alum(KL)	Ferric(KL)	PAC(KL)	Alum(WB)	Ferric(WB)	PAC(WB)
0	17.31	19.02	20.28	13.92	8.63	6.32
3	-	-	43.62	12.16	-	6.55
5	27.87	32.28	48.13	9.21	8.27	7.07
10	30.22	36.01	47.28	10.90	7.8	10.66
15	35.73	35.85	54.03	9.62	7.59	8.94
20	34.66	38.40	60.75	9.02	7.56	8.44
30	40.82	30.62	51.85	13.03	10.87	8.94
40	36.90	38.55	50.69	8.44	11.52	9.31
50	41.19	56.06	31.24	13.62	11.44	11.11
60	48.09	58.89	30.24	8.77	14.84	9.23

Coagulant	mean chord lengths of clays with various coagulant treatments					
conc.						
80	47.73	51.75	33.05	9.95	13.50	9.91
100	43.71	63.29	37.59	10.20	12.77	12.99
150	43.24	56.89	32.80	8.03	13.42	11.46
200	39.88	52.82	-	7.25	17.02	8.42

Table C33 DAF efficency values (%) for kaolin suspensions treated with HTAB.

Recycle ratio	NO addition	1.0E-06	5.0E-06	1.0E-05	2.0E-05
(%)		mol/L	mol/L	mol/L	mol/L
10	24.2	27.0	40.5	58.1	64.7
10	18.2	24.3	39.3	54.8	65.0
20	27.3	29.7	46.4	73.5	76.8
20	24.2	32.4	48.8	73.2	78.2
30	36.4	43.2	57.1	80.0	85.3
30	36.5	43.2	59.5	79.0	86.5
40	45.5	54.0	71.4	87.7	91.2

Table C34 DAF efficency values (%) for kaolin suspensions treated with coagulants and HTAB-coagulants.

Alum	Ferric	PAC	Alum*	Ferric*	PAC*
40(mg/L)	40(mg/L)	10(mg/L)	40(mg/L)	40(mg/L)	10(mg/L)
47.2	56.2	78.9	20.5	47.5	50.0
42.1	56.2	78.2	20.5	45.0	48.0
63.2	61.6	83.4	41.0	66.3	67.6
65.8	63.0	83.9	39.7	66.3	65.7
65.8	65.8	73.7	59.0	78.8	77.4
62.5	64.4	84.5	56.4	77.5	75.5
63.2	64.5	-	-		-
60.5	56.2	83.2	53.8	72.5	68.6
60.5	58.9	82.1	53.8	70.0	68.6
-	-	-	-	83.0	81.7
50.0	48.4	45.9	73.6	80.3	77.6
-	45.2	-	73.6	78.4	77.9
	35.5	45.2 .	73.0	72.2	67.6
-	32.3	-	75.7	72.2	66.2
	Alum 40(mg/L) 47.2 42.1 63.2 65.8 65.8 62.5 63.2 60.5 60.5 - 50.0 - - -	Alum 40(mg/L) Ferric 40(mg/L) 47.2 56.2 42.1 56.2 63.2 61.6 65.8 63.0 65.8 65.8 62.5 64.4 63.2 64.5 60.5 56.2 - - 50.0 48.4 - 45.2 - 35.5 - 32.3	Alum $40(mg/L)$ Ferric $40(mg/L)$ PAC $10(mg/L)$ 47.256.278.942.156.278.263.261.683.465.863.083.965.865.873.762.564.484.563.264.5-60.556.283.260.558.982.150.048.445.9-35.545.2-32.3-	Alum $40(mg/L)$ Ferric $40(mg/L)$ PAC $10(mg/L)$ Alum* $40(mg/L)$ 47.2 56.2 78.9 20.5 42.1 56.2 78.2 20.5 63.2 61.6 83.4 41.0 65.8 63.0 83.9 39.7 65.8 65.8 73.7 59.0 62.5 64.4 84.5 56.4 63.2 64.5 60.5 56.2 83.2 53.8 60.5 58.9 82.1 53.8 $ 50.0$ 48.4 45.9 73.6 $ 35.5$ 45.2 73.0 $ 32.3$ - 75.7	Alum $40(mg/L)$ Ferric $10(mg/L)$ PAC $10(mg/L)$ Alum* $40(mg/L)$ Ferric* $40(mg/L)$ 47.2 56.2 78.9 20.5 47.5 42.1 56.2 78.2 20.5 47.5 42.1 56.2 78.2 20.5 45.0 63.2 61.6 83.4 41.0 66.3 65.8 63.0 83.9 39.7 66.3 65.8 65.8 73.7 59.0 78.8 62.5 64.4 84.5 56.4 77.5 63.2 64.5 60.5 56.2 83.2 53.8 72.5 60.5 58.9 82.1 53.8 70.0 $-$ 83.0 50.0 48.4 45.9 73.6 80.3 $ 45.2$ - 73.6 78.4 $ 35.5$ 45.2 73.0 72.2 $ 32.3$ - 75.7 72.2

* HTAB concentration is 1×10^{-5} mol/L.

Recycle ratio	NO addition	1.0E-06	5.0E-06	1.0E-05	2.0E-05	2.0E-05
(%)		mol/L	mol/L	mol/L	mol/L	mol/L
4	-	-	57.5	-	99.2	-
4	-	-	-	-	98.4	-
6	-	-	65.0	88.0	98 .4	99.9
6	-	-	66.7	87.2	98.8	-
8	7.4	6.9	75.8	95.2	99.8	99.9
8	7.4	10.3	75.0	94.4	-	-
10	11.1	20.7	92.5	93.6	99.8	99.9
10	7.4	17.2	87.5	91.2	-	-
10	-	-	94.8	95.7	-	-
10	-	-	93.9	93.0	-	-
12	7.4	13.8	-	-	-	-
12	11.1	13.8	-	-	-	-
15	14.8	-	70.4	93.9	-	99.9
20	-	26.0	60.0	94.8	99.8	99.9
20	-	25.1	58.3	93.0	-	-
30	-	32.8	40.0	83.5	99.8	-
30	-	31.9	40.9	83.5	-	-

Table C35 DAF efficency values (%) for WB suspensions treated with HTAB.

Table C36 DAF efficency values (%) for WB suspensions treated with coagulants and HTAB-coagulants.

Recycle ratio	Alum	Ferric	PAC	Alum*	Ferric*	PAC*
(%)	40(mg/L)	40(mg/L)	10(mg/L)	40(mg/L)	40(mg/L)	10(mg/L)
6	9.4	20.8	7.4	28.6	7.1	80.8
6	9.4	18.7	7.4	35.7	8.9	80.0
8	18.9	22.9	18.5	57.1	42.9	85.4
8	18.9	25.0	14.8	53.6	39.3	85.4
10	35.8	31.2	10.1	73.1	55.4	91.5
10	28.3	29.1	18.5	65.4	55.4	90.0
10	32.1		18.5	71.4	63.3	-

Recycle ratio	Alum	Ferric	PAC	Alum*	Ferric*	PAC*
(%)	40(mg/L)	40(mg/L)	10(mg/L)	40(mg/L)	40(mg/L)	10(mg/L)
12	28.3	25	14.8	57.1	49.3	80.8
12	24.5	25	11.1	-	-	-
20	23.0		8.8	15.4	43.3	72.2
20	-	-	-	15.4	37.5	72.2
30	18.8	-	9.6	-	8.3	42.6
30	11.6	-	-	-	4.2	43.5

* HTAB concentration is 1 x 10^{-5} mol/L.

Appendix D

Measurement of the horizontal velocity of bubble



Figure D1 The example of bubble diagram from file *.BMP :

The numbers on this figure show the distances from the left hand side of a screen read from a computer programme (Corel Draw). The lower bubble was measured at time t = 0 and the upper bubble was measured at time t = 4 seconds. From the diagram, the grid squares were calibrated by a graticule in which one square represent 58 μ m (or (438-330) = 108 picture scales).

A horizontal positions of the bubbles can be calculated as (371 + 323)/2 = 347 for the lower bubble and (316 + 264)/2 = 290 for the upper bubble.

Then, the horizontal velocity can be calculated as

	=	(347-290)/4
	-	14.25 picture scale/s
or	=	14.25x(58/108) μm/s
	=	7.653 μm/s

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Appendix E

Calculations

E1. Calculating the stationary levels from the Komagata equation

The stationary levels for the Rank Brothers' cell can be obtained from equation (5.1)



$$\frac{s}{0.784mm} = 0.5 - \left[0.0833 + \frac{32(0.784)}{\pi^5(9.34)} \right]$$

s = 0.154 mm

E2. Calculating the electromobility of a bubble

1. Calculate the effective inter electrode distance, l, from

$$l = A_c R_s K_s$$
 [cm]

where A_c is the cross sectional area of rectangular cell = $l_c x d_c$ [cm²], R_s is the resistance = *Volt/current* [ohms] and K_s is the specific conductivity [ohms⁻¹cm⁻¹].

At 25°C, the conductivity of 0.01 mol/L KCl solution is 1405 μ ohms⁻¹cm⁻¹ measured by a PHILIPS conductivity meter model PW9509. When an electric field

was applied at 40V across the cell filled with 0.01 mol/L KCl solution at 25°C, a current can be noted at 0.8 mA and the effective inter electrode distance can be calculated as follows

$$l = (0.0784 \times 0.934)(40/0.8 \times 10^{-3})1405 \times 10^{-6} \text{ cm}$$

= 5.144 cm

2. Calculate the field strength, E_z , from

 $E_z = \frac{applied \ voltage}{l} \quad V/cm$ $= 40/5.144 = 7.776 \quad V/cm$

3. Calculate the electromobility , U_{em} , from

$$U_{em} = \frac{particle \ velocity}{E_Z} \ \mu \, ms^{-1}/Vcm^{-1}$$

for a horizontal velocity = $7.653 \mu m/s$ at 40 V (Appendix D),

$$U_{em} = 7.653/7.776 = 0.984 \ \mu \text{ ms}^{-1}/\text{Vcm}^{-1}$$

E3. Calculating the surface excess concentration from the Gibbs equation

The surface excess concentration can be given in equation (3.36)

$$\Gamma = -\frac{C}{\beta R_g T} \frac{d\gamma_L}{dC}$$
(3.36)

for HTAB solution $C = 1.61 \times 10^{-9} \text{ mol/L}$, $\beta = 1$ and $d\gamma_L/dC = -3.3 \times 10^7 \text{ dyne-cm}^2/\text{mole}$ [14]

at 298 K

$$\Gamma = -\frac{1.61 \times 10^{-9}}{1 \times 8.314 \times 298} (-3.3 \times 10^{7}) \times 10^{-9} \frac{\text{kgmoles}}{\text{m}^{2}}$$
$$= 2.14 \times 10^{-15} \text{ moles/cm}^{2}$$

for $d_p = 27 \,\mu\text{m}$

$$\Gamma A_b = 2.14 \times 10^{-15} \times \pi (27 \times 10^{-4})^2$$
 moles
= 4.9 x 10⁻²⁰ moles

E4. Calculating the surface energy of a solid

The surface tensions of polar and apolar liquids used for contact angle measurements are shown in Table E1.

Liquid	$\gamma_L (mJ/m^2)$	γ_L^{LW} (mJ/m ²)	γ_{L}^{+} (mJ/m ²)	γ_{L} (mJ/m ²)
water	72.8	21.8	25.5	25.5
glycerol	64.0	34.0	3.92	57.4
DIM	50.8	50.8	-	-
BNL	44.4	44.4	-	-

Table E1 Surface tensions of four liquids used for contact angle measurements.

Note DIM = diiodomethane, and BNL = 1-bromonapthalene

For a kaolin surface without chemicals, contact angles were 31.8° measured with distilled water, 29.3° with glycerol, 27.6° with DIM and 23.0° with BNL, respectively. Using equation (6.4), apolar surface energies are given by:

$$1 + \cos\theta = 2\sqrt{\gamma_{s}^{LW} / \gamma_{L}}$$
(6.4)

$$\gamma_{s}^{LW} (\text{DIM}) = \frac{(1 + \cos(27.6))^{2} (50.8)}{4} = 45.18 \text{ mJ/m}^{2}$$
and

$$\gamma_{s}^{LW} (\text{BNL}) = \frac{(1 + \cos(23))^{2} (44.4)}{4} = 40.94 \text{ mJ/m}^{2}$$

$$\gamma_{s}^{LW} (\text{ave}) = 43.06 \text{ mJ/m}^{2}$$

By substituting polar contact angles into equation (6.3), polar surface energies can be obtained:

$$\gamma_L(1+\cos\theta) = 2(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^*\gamma_L^-} + \sqrt{\gamma_S^*\gamma_L^+})$$
(6.3)

For water

$$72.8(1 + \cos(31.8)) = 2(\sqrt{43.06 \times 21.8} + \sqrt{25.5\gamma_s^+} + \sqrt{25.5\gamma_s^-})$$
 (a)

and glycerol

$$64(1 + \cos(29.3)) = 2(\sqrt{43.06 \times 34.0} + \sqrt{57.4\gamma_s^+} + \sqrt{3.92\gamma_s^-})$$
 (b)

The results are $\gamma_s^+ = 1.68 \text{ mJ/m}^2$ and $\gamma_s^- = 35.64 \text{ mJ/m}^2$.

From van Oss [75] the polar surface energy is defined as

$$\gamma_i^{AB} \equiv 2\sqrt{\gamma_i^+\gamma_i^-}$$

Then, the polar energy of the kaolin surface is

$$\gamma_i^{AB} = 2\sqrt{1.68 \times 35.64} = 15.48 \text{ mJ/m}^2$$

and the total surface energy is the sum of polar and apolar surface energies giving 58.54 mJ/m^2 .

From equations (3.49), (6.5), (6.7) and (6.9), the Gibbs' free energies of the kaolin surface are calculated respectively by

$$\Delta G_{131}^{LW} = -2(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}})^2 \qquad (3.49)$$
$$= -2(\sqrt{43.06} - \sqrt{21.8})^2 = -7.17 \text{ mJ/m}^2$$

$$\Delta G_{132}^{LW} = 2(\sqrt{\gamma_1^{LW}} - \sqrt{\gamma_3^{LW}}) \sqrt{\gamma_3^{LW}}$$
(6.5)

$$= 2(\sqrt{43.06} - \sqrt{21.8})\sqrt{21.8} = 17.68 \text{ mJ/m}^2$$

$$\Delta G_{131}^{AB} = -4(\sqrt{\gamma_1^+} - \sqrt{\gamma_3^+})(\sqrt{\gamma_1^-} - \sqrt{\gamma_3^-})$$
(6.7)

$$-4(\sqrt{1.68} - \sqrt{25.5})(\sqrt{35.64} - \sqrt{25.5}) = 13.82 \text{ mJ/m}^2$$

$$\Delta G_{132}^{AB} = 2 \left[\sqrt{\gamma_3^+} (\sqrt{\gamma_1^-} - \sqrt{\gamma_3^-}) + \sqrt{\gamma_3^-} (\sqrt{\gamma_1^+} - \sqrt{\gamma_3^+}) \right] \quad (6.9)$$
$$= 2 \left[\sqrt{25.5} (\sqrt{35.64} - \sqrt{25.5}) + \sqrt{25.5} (\sqrt{1.68} - \sqrt{25.5}) \right]$$
$$= -28.61 \text{ mJ/m}^2$$

The sums of the free energies ΔG_{131}^T and ΔG_{132}^T are 6.65 and -13.34 mJ/m² respectively.

From equations (3.43) and (6.10), the Hamaker constants of kaolin surfaces are calculated as

$$A_{131} = \left(\sqrt{A_{11}} - \sqrt{A_{33}}\right)^2 \tag{3.43}$$

where

$$A_{11} = 6\pi r_{11}^2 \gamma_s^{LW}$$

=

van Oss [75] estimated a value of $6\pi r_{11}^2$ to be 1.86 x 10^{-18} m² so A_{11} for a kaolin surface is 8.01 x 10^{-20} J. By estimating the Hamaker constant of water (A_{33}) to be 3.7 x 10^{-20} J, the Hamaker constants of solid (1), air bubble (2) in water (3) are

$$A_{131} = (\sqrt{8.01 \times 10^{-20}} - \sqrt{3.7 \times 10^{-20}})^2 = 8.21 \times 10^{-21} \text{ J}$$

and

$$A_{132} = (\sqrt{A_{11}} - \sqrt{A_{33}})(-\sqrt{A_{33}})$$
(6.10)
= $(\sqrt{8.01 \times 10^{-20}} - \sqrt{3.7 \times 10^{-20}})(-\sqrt{3.7 \times 10^{-20}}) J$
= $-1.74 \times 10^{-20} J$

E5. Calculating the amount of air concentration

The concentration of air in the saturated liquid can be calculated from Henry's Law as :

$$c = f \frac{P}{K}$$

where c is the concentration of air in the saturated water, P is absolute pressure, f is an efficiency factor and K is Henry's constant which has the value 4.53 kPa/mgL⁻¹ at 25° C [60].

For a pressure of 700 kPa at 25°C and the efficiency factor at 0.8,

$$c = 0.8 \frac{700}{4.53} = 123.62 \text{ mg/L}$$

The water in the column is assumed to be saturated with air at atmosphere pressure so, using an efficiency factor of 1.0, the air concentration can be calculated as

$$c = 1.0 \frac{101}{4.53} = 22.29 \text{ mg/L}$$

For suspension rate at 2 L/min and 10% recycle ratio, the concentration of air released from the saturated water is 101.33 mg/L. Then, the amount of air in a bubble form is given as:

the amount of air released =
$$101.33 \times 0.2 = 20.27$$
 mg/min

Using an air density of 0.001185 g/cm³ at 25°C [139], the amount of air released is 17.09 cm^3 /min and the total flow rate is 0.2171 L/min.

For a column volume of 23.5 L, the amount of air released is given to be 0.181 L. A bubble concentration at 10% recycle ratio gives 2.3 x 10^8 numbers/L. Table E2 shows the air bubble concentration for various recycle ratios.

Recycle ratio(%)	Amount of air released (L)	Bubble concentration (nums/ m^3)
6	0.1131	1.44 x 10 ¹¹
8	0.1478	1.88 x 10 ¹¹
10	0.1812	2.30 x 10 ¹¹
12	0.2132	2.71 x 10 ¹¹
20	0.3302	4.19 x 10 ¹¹
30	0.4538	5.76 x 10 ¹¹
40	0.5579	7.08 x 10 ¹¹

Table E2 Amount of air released and bubble concentrations in the flotation column.

E6. Calculating the flotation efficiency

From the flotation model, the trajectory model, described in Appendix H, a critical radius or limiting trajectory, l_L , can be given as shown:



Where h is the distance between a particle and a bubble measured between surfaces and r is the distance between a particle and a bubble measured between centres. The limiting trajectory, l_L , can be calculated as :

$$l_L = r \sin \alpha$$

= $(h + r_p + r_b) \sin \alpha$

From equation (4.17), a particle capture efficiency per bubble, η_{Tc} , is calculated using the limiting trajectory as :

$$\eta_{Tc} = (l_L / r_b)^2$$
 (4.17)

and the flotation efficiency can be determined by equation (3.9) for the continuous flotation process.

$$1 - \frac{N_p}{N_{p0}} = 1 - \exp\{(-\eta_{Tc})(A_b u_b N_b)\tau\}$$
(3.9)

where τ is the retention time obtained from total column volume divided by total fluid flow rate, which can be summarised as follows:

%Recycle ratio	6	8	10	12	20	30	40
τ (s)	662	649	636	624	579	532	489

Where there is no floc breakage due to shear gradients, for example, kaolin suspension treated with HTAB at a concentration of 1 x 10⁻⁶ mol/L, the calculation gives α to be 0.0012 using $r_p = 6.5 \times 10^{-6}$ m, $r_b = 20.0 \times 10^{-6}$ m and h_0 at 100 r_p

(where h_0 is the separation distance at $\tau = 0$). From equations (4.17) and (3.9), at 10% recycle ratio ($N_b = 2.3 \times 10^{11} \text{ nums/m}^3$, $u_b = 8.7 \times 10^{-4} \text{ m/s}$ and $\tau = 636 \text{ s}$), the particle capture efficiency per bubble, η_{Tc} , is 0.00165 and the flotation efficiency is 23.2%. Table E3 shows results obtained from kaolin and Wyoming bentonite treated with HTAB in the case of floc sizes unchanged by shear.

Clay	HTAB concentration	$r_p \ge 10^6$	α	$l_L \ge 10^6$	η _{Tc} ,
	(mol/L)	(m)	(radian)	(m)	(-)
kaolin	1 x 10 ⁻⁶	6.5	0.0012	0.811	0.0016
	5 x 10 ⁻⁶	6.7	0.0018	1.263	0.0034
	1 x 10 ⁻⁵	7.0	0.0022	1.606	0.0064
	2 x 10 ⁻⁵	7.1	0.0028	2.072	0.0107
WB	1 x 10 ⁻⁶	6.3	0.0012	0.811	0.0016

Table E3 Flotation parameters for the trajectory model.

For floc sizes that are affeced by increasing recycle ratios, for example Wyoming bentonite suspension treated with HTAB in the concentration range of 5 x 10^{-6} to 3 x 10^{-5} mol/L, the flotation efficiencies are shown in Table E4.

Table E4 Flotation parameters for the trajectory model for Wyoming bentonite suspensions treated with HTAB in the concentration range of 5 x 10^{-6} to 3 x 10^{-5} mol/L.

HTAB conc.	Recycle	$r_p \ge 10^6$	α	η _{Τc} ,	Flotation
(mol/L)	ratio (%)	(m)	(radian)	(-)	eff. (%)
5 x 10 ⁻⁶	6	8.0	0.0024	0.0099	64.2
	8	7.6	0.0024	0.0089	69.5
	10	7.4	0.0024	0.0085	74.3
	20	6.3	0.0018	0.0035	60.4
	30	5.9	0.0014	0.0019	46.4

HTAB conc.	Recycle	$r_p \ge 10^6$	α	η _{Τc} ,	Flotation
(mol/L)	ratio (%)	(m)	(radian)	(-)	eff. (%)
1 x 10 ⁻⁵	6	13.3	0.0028	0.0364	97.7
	8	12.4	0.0028	0.0317	98.5
	10	11.7	0.0028	0.0283	98.9
	20	9.8	0.0028	0.0199	99.5
	30	8.1	0.0026	0.0109	97.4
2 x 10 ⁻⁵	10	29.7	0.0022	0.1103	99.9
	20	26.8	0.0022	0.0900	100
	30	23.9	0.0022	0.0717	100
3 x 10 ⁻⁵	10	38.6	0.0024	0.2211	100
	20	36.9	0.0024	0.2022	100
	30	35.1	0.0024	0.1830	100
5 x 10 ⁻⁵	10	42.0	0.0020	0.1816	100
	20	41.2	0.0020	0.1748	100
	30	40.3	0.0020	0.1673	100

E7. Calculating an attachment efficiency

The attachment efficiency may be calculated using a proposed equation (9.6) and the maximum free energy at equilibrium, W_{132} , for material (1) attaching to material (2) in medium (3) as given in equation (9.5).

$$\eta_a = \exp\left(-\frac{E_1}{S_c W_{132}}\right) \tag{9.6}$$

$$W_{132} = \gamma_{LV} (1 - \cos\theta) \tag{9.5}$$

where γ_{LV} is the surface tension of water-air interface in this case, θ is the contact angle measured using water and S_c is the contactable surface area (for HTAB molecules, Chen and co-workers found that the contactable surface area was 6.5 nm² [128]).

For kaolin suspensions treated with HTAB at a concentration of 1 x 10^{-6} mol/L, a contact angle value on a solid surface using drop water was 50.4° . Taking the surface tension of water to be 72.8 mJ/m², the maximum free energy at equilibrium, W_{132} , is 26.39 mJ/m² and, S_cW_{132} is 1.12 x 10^{-18} J. The attachment efficiency is 0.65. The results were shown in Table 9.2.

E8. Calculating a flotation efficiency using the mixing zone model

Equation (9.3) can be used to determine a coefficient constant, a_1 , using a fitting technique.

$$\frac{\mathrm{d}N_p}{\mathrm{d}t} = -a_1 \sqrt{\frac{P_{in}}{\mu V}} (d_b + d_p)^3 \eta_a N_b N_p \qquad (9.3)$$

For kaolin suspensions treated with HTAB, attachment efficiency values were shown in Table 9.2, bubble concentrations shown in Table E2, shear gradients shown in Table G2, particle diameters shown in Table E3 and bubble diameter taken as 40 μ m. The results for the best fit of the coefficient constant was shown in Figures 9.30-9.33. For Wyoming bentonite suspensions treated with HTAB, fitted results were represented by Figures 9.34-9.37.

Appendix F

Design of pilot-scale DAF rig

This section describes the design calculations for the DAF rig including the coagulation and flocculation section, and sets out the operating conditions.

F.1 Flotation column

An 80 mm inside diameter Perspex tube 3 metres long was used for the pilot scale flotation column and the maximum Reynolds number in laminar flow was used to calculate the upper limit of suspension flow rate in the column as follows.

Basis: Re = 2,300, water density 1000 kg/m³, water viscosity 10⁻³ Pa-s and column diameter 80 mm.

Assuming suspension mixture in flotation column as liquid water, then

$$Re = \frac{\rho_w v d_{col}}{\mu}$$

where d_{col} is the column diameter.

J

$$2300 = \frac{(1000)v(0.08)}{10^{-3}}$$

$$v = 0.02875 \text{ m/s}$$

$$v = \frac{flowrate}{area}$$

$$flow rate = 0.02875 \pi \frac{(0.08)^2}{4} \text{ m}^3/\text{s}$$

$$= 1.44513 \times 10^4 \text{ m}^3/\text{s}$$

=

From

8.67 L/min

This flow rate is the maximum value for the mixture including air bubbles in flotation column. The recycle ratio is normally set in the range of 10-30 % by volume of the feed mixture. Then,

recycle flow rate = $8.67 \times 0.3 \text{ L/min}$ = 2.601 L/min

The concentration of air in the saturated liquid can be calculated from Henry's Law in the form

$$c = f \frac{P}{K}$$

where c is the concentration of air in the saturated water, P is absolute pressure, f is an efficiency factor given as 0.9 for packed saturators and K is Henry's constant which has the values 2.72 and 4.53 kPa/mgL⁻¹ at 0 and 25°C respectively [60]. For a pressure of 700 kPa at 25°C, the air concentration is 139.07 mg/L.

The water in the column is assumed to be saturated with air at atmosphere pressure so, using an efficiency factor of 1.0, the air concentration is 22.29 mg/L. The concentration of air released from the saturated water is 116.78 mg/L.

Then, the amount of air in a bubble form is given as

the amount of air released = $116.78 \times 2.601 \text{ mg/min}$ = 303.75 mg/min

Using an air density of 0.001185 g/cm³ at 25°C [139] gives the amount of air released = $303.75 \times 10^{-3} / 0.001185 \text{ cm}^3 / \text{min}$ = $256.33 \text{ cm}^3 / \text{min}$ The terminal velocity of bubbles of about 35 μ m was reported to be 0.05 cm/s [14]. This bubble terminal velocity is negligible when it is compared with mixture velocity in the flotation column (2.875 cm/s). Then, the suspension flow rate from flocculator could be given as

suspension rate	=	mixture flow rate - recycle rate - air rate
	=	8.67 - 2.601 - 0.256 L/min
	=	5.81 L/min
	≈	6 L/min

This gives an extreme upper limit to the flowrate. The flowrate and recycle ratios used in the experiments were 2 L/min and 6-40%, respectively.

F.2 Stock suspension tank or feed tank

The pilot scale DAF rig was intended to be operated in semicontinuous mode for at least 3 hours operation. The feed tank volume can be calculated simply as follows:

Volume	=	Suspension flow rate x time
	=	6 L/min x 3 x 60 min
	=	1,080 L
	~	1000 L

From a general design standpoint, a 1 m³ feed tank would usually have a four bladed stirrer with the total projected area of the blades less than 20% of the cross-sectional tank area [140] and velocity gradients varying in the range of 40-150 s⁻¹. In this case the shear gradient was based on an average value of 100 s⁻¹ and the stirrer geometry based a blade area on 15% of the total area and 80% of liquid tank volume. The dimensions and operating conditions of the feed tank are summarised in Table F.1.

Basis: the tank with a four paddle stirrer gives a ratio of stirrer diameter to tank diameter of 0.6 and a projected blade area of 15% of the cross-sectional tank-area. Liquid volume was 1,000 litres and tank volume was 1,250 litres (80% liquid operation). Velocity gradient was 100 s⁻¹.

1. Tank diameter

Volume =
$$\frac{\pi D_T^2 L_T}{4}$$

where L_T is the height of liquid in the tank assumed to be equal to its diameter D_T .

$$D_T = \sqrt[3]{\frac{1000x10^{-3}(4)}{\pi}} \text{ m}$$

= 1.08 m

2. Tank height

Tank height =
$$\frac{1,250 \times 10^3 \times 4}{\pi (108^2)}$$
 = 136.4 cm
= 1.36 m

3. Power

$$G = \sqrt{\frac{P_{OT}}{Volume \times \mu}}$$

$$P_{OT} = (100)^{2} \times 1,000 \times 10^{-3} \times 10^{-3} \text{ Pa-cm}^{3}\text{-s}^{-1}$$

$$= 10.0 \text{ N-m-s}^{-1}$$

4. Paddle dimensions

Cross-sectional tank-area =
$$\frac{\pi (1.08)^2}{4} m^2$$

= 0.916 m²
Total blade area = 0.15 x 0.916 m²
= 0.1374 m²

For a four bladed stirrer, each blade 0.8 m long (about 80% liquid height)

Single blade area	=	0.1374/4 m ²
Width of each blade	=	0.043 m
	≈	0.04 m

5. Stirrer speed [141]

$$P_{OT} = \frac{C_D \rho_w (v_p - v)^3 A_p}{2}$$

where $(v_p - v)$ is the relative velocity of the liquid to the paddle blade assumed to be about 0.8 [141] of the paddle mean velocity, v_p is the paddle mean velocity, C_D is a drag coefficient taken as 1.5 and A_p is the total projected area of paddles. Then,

$$(v_{p} - v) = \sqrt[3]{\frac{10x2}{1.5 \times 1000 \times 4 \times (0.8x0.038)}} = 0.4786 \text{ m/s}$$

and
$$(v_{p} - v) = 0.8 v_{p}$$

$$v_{p} = 0.4786/0.8 = 0.5982 \text{ m/s}$$

paddle speed = $\frac{0.5982}{2\pi} = 0.0952 \text{ rps}$
= 5.7 rpm

6. Reynolds number of stirred tank

Re =
$$\frac{(0.6)^2 \times 0.0952 \times 1000}{10^{-3}}$$

= 34,272

Parameter	Feed tank
Liquid volume [litres]	1,000
Residence time [hr]	3
Tank diameter [m]	1.08
Tank height [m]	1.36
<i>G</i> [s ⁻¹]	100
Gt [-]	$1.08 \ge 10^6$
Stirrer type	4 paddles (wide/diameter = 20)
Stirrer length [m]	0.8
Stirrer wide [m]	0.04
Stirrer diameter [m]	0.6
Stirrer speed [rpm]	6
Re [-]	34,272

Table F.1 Dimensions and operating conditions of the feed tank.

F.3 Flocculator design

The feed tank was used for both rapid and slow mixing based on the average shear rates of 250 s⁻¹ for rapid mixing and 100 s⁻¹ for flocculation [3, 48-52, 142-144]. Table F.2 gives the operating conditions calculating for an operating volume based on 80% of tank volume.

F.4 Flotation tank

A flotation tank usually has an average overflow rate or hydraulic loading rate of 7 m/hr and an average detention time of 10 min [60,144-146].

The effective area of the flotation tank can be calculated as follows:

Hydraulic loading rate=	mixture rate/area
Area of flotation tank =	$\frac{8.67 \times 10^{-3} \times 60}{7} \text{ m}^2$
=	0.0743 m^2

Table F.2 Dimensions and operating conditions for rapid mixing and flocculation tank.

Rapid mixing tank	Flocculator
1.08	1.08
1.36	1.36
250	100
30,000	1.8×10^5
4 paddles	4 paddles
(width/diameter=20)	(width/diameter=20)
0.6	0.6
20	6.0
120,000	34,272
	Rapid mixing tank 1.08 1.36 250 30,000 4 paddles (width/diameter=20) 0.6 20 120,000

F.5 Summary

The maximum flowrate of the suspension in the flotation column at the limit of laminar flow was calculated to be about 6 L/min. The suspension flowrate, however, used in the experiments was 2 L/min on every run. The feed tank was designed for use as a rapid mixing and flocculation tank by regulating the motor speed. The tank was fitted with 4 baffles and a 4-paddle agitator connected to a gear box that could vary the agitator speed in the range of 0-20 rpm. The ratio of baffle width to tank diameter was 0.1 while the total paddle area was 15 % of the cross-sectional tank area. The cross-sectional area of the flotation tank was about 0.08 m², assuming a hydraulic loading rate of 7 m/hr, and the retention time was 2 min for the contacting zone and 10-30 min for the separating zone.







Appendix G

Power correlation for floc breakup tests

Floc breakage in a flotation column results in a decrease in flotation efficiencies. Energy dissipation from an injection of saturated water can be estimated and compared to a result obtained from the floc break-up tests described in Chapter 7. Torque measurements for a stirred tank were described in Chapter 5 and an apparatus was shown in Figure 5.6. Tap water was added until it reached the standard tank configuration i.e. liquid height = tank diameter. After switching on the motor, its speed was measured using a tachometer. When the motor speed was constant, the weight on the platform scale was noted.

G.1 Power calculation

The raw-data relationship between motor speed (X-axis) and the weight obtained from the platform scale is shown in Figure G1.





G.2 Power correlation

Using a regression technique, a correlation between the agitator speed and the weight was obtained and is shown in Table G1.

Table G1 Second order polynomial equations relating the agitator speed (X-axis) to the weight (Y-axis).

Line	Equation	R ²
Power1	$Y = 1E - 04x^2 + 0.041x - 3.0146$	0.98
Power2	$Y = 1E - 04x^2 - 0.021x + 0.2512$	0.94

The agitator power, P_{in} , can be calculated from in equation (G1):

$$P_{in} = 2\pi \times \text{RPS} \times \text{Torque}$$
 (G1)

where RPS is the agitator speed (revolution per second) and the Torque is the force multiplied by the arm radius (7 cm). Figure G2 shows the results obtained from a calculation of the mixing power or the power per unit volume for a stirred tank as described in Chapter 5.





The floc break up tests described in Chapter 7 showed relationships between shear gradients and mean particle sizes. Using this correlation, floc breakage in a flotation column can be estimated through a comparison with the calculated shear force of the saturated water released in the flotation column.

G.3 Energy dissipation from a submerged nozzle

Figure G3 shows a mixing zone for a nozzle submerged in a column. Cramers and co-workers [147, 148] defined the effective volume of the mixing zone as a conical volume of a jet where its perimeter reaches the column wall.



Figure G3 A nozzle submerged in a column showing a mixing zone in the flotation column where L_{MZ} is the mixing zone length.

The energy dissipation of the nozzle submerged in the column can be given in equation (G1).

$$\frac{P_J}{V_{MZ}} = \frac{M u_{noz}^2}{2V_{MZ}}$$
(G1)

where P_J is the jet power, V_{MZ} is the mixing volume, u_{noz} is the fluid velocity at a nozzle, d_{noz} is the nozzle diameter and M is the mass flow rate.

The mixing zone length is a function of the operating conditions and geometrical parameters of the nozzle. Observations from the experiments show the mixing zone length in the range of 20 to 40 cm. Thus, it is possible to assume the mixing zone length to be 30 cm.

The energy dissipation in the present work may obtain from the saturated water stream, the suspension stream and the air released. The flotation column was placed on a plate drilled with two nozzles 6 and 8 mm diameter and situated at the centre and at 30 mm radius as described in Chapter 5.

For a suspension inlet flow of 2 L/min giving a suspension velocity of 0.6627 m/s for the 8 mm orifice diameter, the power per unit volume obtained from equation (G1) can be calculated as:

$$\frac{P_J}{V_{MZ}} = \frac{0.0333 \times (0.6627)^2}{2\frac{\pi}{4} \times 0.1 \times 0.1 \times 0.3} = 3.105 \text{ W/m}^3$$

For the 6 mm nozzle diameter and a saturated water velocity of 0.12 m/s for a 10% recycle ratio, the power per unit volume obtained from equation (G1) can be calculated to be 0.01 W/m^3 .

Further energy dissipation may come from the air bubbles released and this energy can be given as:

$$\frac{P_{in}}{V_{col}} = \frac{Q_M}{V_{col}} \rho_L g H_t$$
(G2)

where P_{in} is the power, V_{col} is the volume of flotation column, Q_M is the volumetric flow rate of air, ρ_L is the liquid density and H_t is the column height.

For a 10% recycle ratio, the energy dissipation can be calculated as:

$$\frac{P_{in}}{V_{col}} = \frac{0.00028(L/s)}{23.5(L)} \times 998 \times 9.8 \times 3 = 0.356 \text{ W/m}^3$$

The total energy dissipation is the sum of the energies from the saturated water, the suspension stream and the air released. These total energies are compared to the mixing power values obtained from the stirred tank as given in Figure G2. The agitator speeds are listed in Table G2.

Table G2 Relationships between the dissipation energy, calculated from the suspension stream and the saturated water injection stream, and agitator speed obtained from the mixing tank calculations as shown in Figure G2.

Recycle ratio (%)	Power/volume (watt/L)	Agitator speed (RPM)
4	0.0032	105
6	0.0033	110
8	0.0034	112
10	0.0035	115
12	0.0036	117
20	0.0039	120
30	0.0044	125
40	0.0052	130

These agitator speeds were used to determine the particle or floc sizes at given shear gradients, from the relationship between agitator speeds and floc sizes in Tables C13 and C14.

Appendix H

Modelling programme

H.1 Coagulation model

The extended-DLVO theory was used to model the coagulation of the clay suspensions treated with chemicals as described in Chapter 7. The computer programme for the extended-DLVO theory was written using BASIC language shown in the programme list P1. The total energies containing electrostatic (V_{E1}), van der Waals (V_{A1}) and hydrophobic (V_{H1}) energies were calculated using the interactions based on two spherical particles as given in equations (H1) to (H3).

$$V_{E1} = 2\pi\varepsilon\varepsilon_0 r_p \zeta_p^2 \ln(1 + \exp(-\kappa h))$$
(H1)

$$V_{A1} = -\frac{A_{131}r_p}{12h}$$
(H2)

$$V_{H1} = \pi r_{\rho} \lambda_{L} \Delta G_{131}^{AB} \exp(\frac{h_{0} - h}{\lambda_{L}})$$
(H3)

where r_p is the particle radius, ε is the dielectric constant, ε_0 is the permittivity at free space = 8.854 x 10⁻¹² F/m, κ is the reciprocal thickness of the double layer, ζ_p is the zeta potential of particles, h is the separation distance, h_0 is the minimum equilibrium distance that is estimated as 0.16 nm [75] and λ_L is the decay length (normally are in the range of 1-2 nm [104, 149-154] for short range forces and 10-15 nm for a long range force [155]).

For the electrostatic energy, the zeta potential values for clay suspensions as given in section 6.3 were used in the model. The Hamaker constants (A_{131}) as shown in Table 6.13 and the free energies, ΔG_{131}^{AB} , as exhibited in Tables 6.9 to 6.12 were used to

calculate the van der Waals and the hydrophobic energies (or hydration energy), respectively.

The reciprocal thickness of the double layer, κ , shown in equation (3.13) can be simply calculated using equation (H4) at 25°C [63] as

$$\kappa = 3.29\sqrt{I} \qquad [nm^{-1}] \tag{H4}$$

where I is the ionic strength $(I = \sum_{i} C_i Z_i^2)$, C_i is the ion concentration of component i

and Z_i is the charge of the ion *i*. From Appendix B, the ionic strength of tap water used for the preparation of the clay suspensions in the present experiments contains calcium (1.231 mmol/L), magnesium (0.393 mmol/L), sodium (1.045 mmol/L), and potassium ions (0.072 mmol/L). Then, the reciprocal thickness of the double layer for tap water is 0.2855 nm⁻¹.

Programme list P1 for the coagulation model.

```
REM This section calculates attachment forces using extended-DLVO
REM
        theory.
REM
     DIM dist(100): DIM elecf(100)
     DIM VANF(100): DIM hydrof(100): DIM TOTAF(100)
  CLS
    PRINT "This programme investigates extended-DLVO theory"
    PRINT " for the coagulation of clay suspensions"
    PRINT " treated with coagulants."
    PRINT
    dist(0) = 0
    GOTO 300
30
    FOR I = 1 TO 50
     GOSUB 500
     TOTAF(I) = elecf(I) + VANF(I) + hydrof(I)
     PRINT "TOTAF"; TOTAF(I)
     OPEN "a:bh3e5.dat" FOR OUTPUT AS #1
     PRINT #1, "Zeta potential", zetap, "mV"
     PRINT #1, "Parcicle diameter", DIAP, "micron"
```

```
PRINT #1, "Hamaker constant", HAMC, "J"
     PRINT #1, "Polar energy", GAB, "J/m^2"
     PRINT
     PRINT #1, "Distance", "ELECF", "VANF", "TOTAF(J)"
     FOR J = 1 TO 50
     PRINT #1, dist(J), elecf(J), VANF(J), hydrof(J), TOTAF(J)
     NEXT J
     CLOSE #1
     NEXT I
END
300 REM
            Electrostatic force (input data)
  REM
  REM
    PRINT "Electrostatic force": PRINT
    INPUT "Zeta potential of particle (mV) = "; zetap
    INPUT "Particle diameter (micron) = "; DIAP
    RIAP = DIAP * .000001 / 2
    kapa = .2855 / 1E-09
    die = 78.54 * 8.854E-12
    dist = 0
  REM
  REM
            Van der waals force (input data)
  REM
410 CLS
    PRINT "Van der Waals force for two spheres (input data)"
    PRINT
    INPUT "Hamaker constant (J)"; HAMC
    PRINT
  REM
           Hydrophobic force (input data)
  REM
  REM
420 CLS
    PRINT "Hydrophobic force (input data)"
    PRINT
    INPUT "Polar free energy (J/m^2)"; GAB
    PRINT
  GOTO 30
500
REM
REM
             Electrostatic force (cal.)
REM
    dist(I) = dist(I - 1) + 5E-10
    el1 = -(kapa * dist(I))
    el2 = (zetap ^ 2) * .000001
```
```
el3 = 1 + EXP(el1)
    EE1 = LOG(el3)
    elecf(I) = 2 * (22 / 7) * die * RIAP * el2 * EE1
     PRINT "Electrostatic force"; elecf(I); "J"
510
REM
REM
            Van der waals force 1 (cal.)
REM
    VANF(I) = -(HAMC * RIAP / (12 * dist(I)))
     PRINT : PRINT "Van der waals force"; VANF(I); "(J)"
520
REM
REM
            Hydrophobic force (cal.)
REM
    hyd1 = ((1.6E-20) - dist(I)) / 1E-09
    hyd2 = EXP(hyd1)
    hydrof(I) = (22 / 7) * RIAP * 1E-09 * GAB * hyd2
    PRINT "Hydrophobic force"; hydrof(I); "J"
    RETURN
REM
REM
END
```

H.2 Interfacial forces between bubbles and particles

The extended-DLVO theory was also used to describe interfacial forces between bubbles and particles for clay suspensions treated with chemicals as described in Chapter 8. The computer programme for the extended-DLVO theory was written using BASIC language shown in the programme list P2. The total energies for particles interacting with bubbles, comprising electrostatic (V_{E2}), van der Waals (V_{A2}) and hydrophobic (V_{H2}) energies, were calculated using the interactions based on two spherical objects as given in equations (H4) to (H6).

$$V_{E2} = 4\pi\varepsilon\varepsilon_0 r_p \zeta_p \zeta_b \left(\frac{\exp(-\kappa h)}{1+\exp(-\kappa h)}\right)$$
(H4)

$$V_{A2} = -\frac{A_{132}r_pr_b}{6(r_p + r_b)h}$$
(H5)

$$V_{H2} = 2\pi \left(\frac{r_p r_b}{r_p + r_b}\right) \lambda_L \Delta G_{132}^{AB} \exp(\frac{h_0 - h}{\lambda_L})$$
(H6)

where ζ_p is the zeta potential of particles, ζ_b is the zeta potential of bubbles, r_b is the bubble radius, A_{132} is the Hamaker constants for surfaces (1) and (2) in water (3) as shown in Table 6.13 and ΔG_{132}^{AB} is the free energies for surfaces (1) and (2) in water (3) as exhibited in Tables 6.9 to 6.12.

Programme list P2 for bubble-particle attachment forces.

```
REM EXDLVO3.BAS
REM This section calculates attachment forces using
REM
        extended-DLVO theory.
REM
     DIM dist(100): DIM elecf(100)
     DIM VANF(100): DIM hydrof(100): DIM TOTAF(100)
  CLS
    PRINT "This programme investigates extended-DLVO theory"
    PRINT " for the attachment of clay suspensions"
    PRINT " in a flotation model."
    PRINT
    dist(0) = 0
    Pi = 22 / 7
    GOTO 300
30
    FOR I = 1 TO 50
     GOSUB 500
     TOTAF(I) = elecf(I) + VANF(I) + hydrof(I)
     PRINT "TOTAF"; TOTAF(I)
     OPEN "a:kh1e55.dat" FOR OUTPUT AS #1
     PRINT #1, "06 July 99"
     PRINT #1, "Zeta potential of particle", zetap, "mV"
    · PRINT #1, "Zeta potential of bubble", zetab, "mV"
     PRINT #1, "Particle diameter", DIAP, "micron"
     PRINT #1, "Hamaker constant", HAMC, "J"
     PRINT #1, "Polar energy", GAB, "J/m^2"
     PRINT
     PRINT #1, "Distance", "ELECF", "VANF", "TOTAF(J)"
     FOR J = 1 TO 50
     PRINT #1, dist(J), elecf(J), VANF(J), hydrof(J), TOTAF(J)
     NEXT J
     CLOSE #1
```

NEXT I **END** 300 REM REM Electrostatic force (input data) REM PRINT "Electrostatic force": PRINT INPUT "Zeta potential of particle (mV) = "; zetap INPUT "Zeta potential of bubble (mV) = "; zetab INPUT "Particle diameter (micron) = "; DIAP INPUT "Bubble diameter (micron) = "; DIAB RIAP = DIAP * .000001 / 2RIAB = DIAB * .000001 / 2kapa = .2855 / 1E-09die = 78.54 * 8.854E-12 dist = 0REM REM Van der waals force (input data) REM 410 CLS PRINT "Van der Waals force for two spheres (input data)" PRINT INPUT "Hamaker constant (J)"; HAMC PRINT REM REM Hydrophobic force (input data) REM 420 CLS PRINT "Hydrophobic force (input data)" PRINT INPUT "Polar free energy (J/m^2)"; GAB PRINT **GOTO 30** 500 REM Electrostatic force (cal.) REM REM dist(I) = dist(I - 1) + 5E-10ell = -(kapa * dist(I))el2 = (zetap * zetab) * .000001 el3 = 1 + EXP(el1)el4 = 4 * EXP(el1)EE1 = el4 / el3elecf(I) = Pi * die * RIAP * el2 * EE1 PRINT "Electrostatic force"; elecf(I); "J"

```
510
REM
REM
            Van der waals force 1 (cal.)
REM
    VANF(I) = -(HAMC * RIAP * RIAB / (6 * (RIAP + RIAB) * (dist(I))))
     PRINT : PRINT "Van der waals force"; VANF(I); "J"
520
REM
REM
           Hydrophobic force (cal.)
REM
    hyd1 = ((1.6E-20) - dist(I)) / 1E-09
    hyd2 = EXP(hyd1)
    hyd3 = RIAP * RIAB / (RIAP + RIAB)
    hydrof(I) = 2 * Pi * hyd3 * 1E-09 * GAB * hyd2
    PRINT "Hydrophobic force"; hydrof(I); "J"
    RETURN
REM
REM
END
```

H.3 Flotation model

The computer programme for the flotation model was written using BASIC language shown in the programme list P3. From Chapter 4, the critical trajectories were calculated using hydrodynamic and interfacial energy terms comprising electrostatic (V_{E2}) , van der Waals (V_{A2}) and hydrophobic (V_{H2}) energies based on two spherical objects as given in equations (H7).

$$\frac{dH}{d\alpha} = \frac{f_1}{6\pi\mu r_p^2} \frac{2(1+HR+R)^2}{3R^2(H+1)u_B f_3 \sin\alpha} \left\{ -\frac{A_{132}}{6r_p H^2} + \pi\varepsilon r_p \kappa \zeta_p \zeta_b \right\} \\ \left[\frac{4\exp(-\kappa r_p H)}{\left\{ 1+\exp(-\kappa r_p H) \right\}} \right] + 2\pi \frac{r_p r_b}{r_p + r_b} \Delta G_{132}^{AB} \exp(\frac{h_0 - Hr_p}{\lambda_L}) \\ -\frac{3R^2(H+1)^2}{2(1+HR+R)^2} 6\pi\mu r_p u_B f_2 \cos\alpha \right\}$$
(H7)

where f_1 , f_2 , and f_3 were determined using empirical equations as given in equations (H8) to (H10).

$$f_1, = \frac{1.10337H^{0.94}}{1.19113 + H^{0.94}}$$
(H8)

$$f_2$$
, = 1.58576exp(-1.21*H*) + 1.50628exp(-0.033*H*) (H9)

$$f_3 = \frac{1.02813H^{0.73}}{0.073885 + H^{0.73}}$$
(H10)

Programme list P3 for flotation model.

CLS

REM RUNGE KUTTA Method DIM X0(1200): DIM Y0(1200) DIM X(1200): DIM Y(1200): DIM F(1200) DIM PARP(1200) DIM EQM1(1200): DIM EQM2(1200): DIM EQM3(1200) DIM hyddf1(1200): DIM hyddf2(1200) DIM VANF(1200): DIM ELECF(1200): DIM HYDFF(1200) DIM ELECF1(1200): DIM ELECF2(1200): DIM elecf3(1200) DIM TOTF(1200)

```
REM ***** Initialise *****
READ X0(1), Y0(1), XF
    H = .001
    Pi = 22 / 7
    RIAP = 6.33 * .000001
    RIAB = 20 * .000001
    R = RIAP / RIAB
    vis = .001
    KAPA = .2855 / 1E-09
    ZETAP = -23.6
    ZETAB = 31
    A132 = -1.5E-20
    G132 = -.03287
  REM ***** STEP ******
110 FOR I = 1 TO 1500
    PRINT X0(I), Y0(I)
    OPEN "d:bh1e610.dat" FOR OUTPUT AS #1
    PRINT #1, "From model2.bas; 14 July 1999"
    PRINT #1, "Zeta potential of particle", ZETAP
```

```
PRINT #1, "Zeta potential of bubble", ZETAB
    PRINT #1, "Hamaker constant", A132
    PRINT #1, "Polar energy", G132
    PRINT #1, "Particle radius", RIAP
    PRINT #1, "X0", , "Y0"
    FOR J = 1 TO 1200
    PRINT #1, X0(J), , Y0(J)
    NEXT J

    CLOSE #1

    IF X0(I) > XF - .0000001 THEN END
    YCON = 5E-09 / RIAP
    IF YO(I) < YCON THEN END
    X(I) = X0(I)
    Y(I) = YO(I)
    GOSUB 900
    K1 = H * PARP(I)
    X(I) = X0(I) + H / 2
    Y(I) = Y0(I) + K1 / 2
    GOSUB 900
    K2 = H * PARP(I)
    Y(I) = Y0(I) + K2 / 2
    GOSUB 900
    K3 = H * PARP(I)
    X(I) = X0(I) + H
    Y(I) = Y0(I) + K3
    GOSUB 900
    K4 = H * PARP(I)
    X0(I + 1) = X(I)
    Y0(I + 1) = Y0(I) + (K1 + 2 * (K2 + K3) + K4) / 6
    NEXT I
    PRINT "error"
    END
800 REM*****INITIAL X, INITIAL Y, FINAL X*****
    DATA .0012,100,1.6
900
     REM****DEFINE F(X,Y)*****
    GOSUB 1000
    GOSUB 1200
    GOSUB 1300
    PARP(I) = EQM2(I) * (TOTF(I) - hyddf2(I))
    RETURN
1000 REM ***** Term of equation of motion *****
    fac1 = 1.10337 * (Y(I)) ^ .942634 / (1.19113 + (Y(I)) ^ .942634)
    PRINT I
REM
         IF Y(I) < .1 THEN fac I = Y(I)
    fac3 = 1.02813 * (Y(I)) ^ .727365 / (.073885 + (Y(I)) ^ .727365)
```

```
IF Y(I) < .1 THEN fac3 = (.7431 / (.6376 - .2 * ln(Y(I))))
    GOSUB 1100
    EQM1(I) = (2 * ((1 + Y(I) * R + R)^{2})) / (3 * R^{2} * (Y(I) + 1))
    EQM2(I) = EQM1(I) * fac1 / (6 * Pi * RIAP * .001 * UB * SIN(X(I)) * fac3)
REM
         PRINT Y(I)
REM
         PRINT "EQM1="; EQM1(I)
REM
         PRINT "EQM2="; EQM2(I)
    RETURN
1100 REM ***** Bubble velocity (Stoke's law) *****
    UB = (9.8 * 998 / (18 * vis)) * ((RIAB * 2)^2)
    RETURN
1200 REM ***** Hydrodynamic force *****
    fac2 = 1.58576 * EXP(-1.21233 * Y(I)) + 1.50628 * EXP(-.0328751 * Y(I))
    IF Y(I) \ge 10 THEN fac2 = 1.1544
    IF Y(I) < .1 THEN fac2 = 3.23
    hyddfl(I) = (3 * (R^2) * ((Y(I) + 1)^2)) / (2 * ((1 + Y(I) * R + R)^2))
    hyddf2(I) = hyddf1(I) * 6 * Pi * vis * RIAP * UB * COS(X(I)) * fac2
    RETURN
1300 REM ***** Total surface forces *****
  REM ***** van der Waals *****
    VAN1 = (RIAP * RIAB) / (RIAP + RIAB)
    VANF(I) = -A132 / (6 * VAN1 * (Y(I))^2)
    PRINT "van der Waals force"; VANF(I); "N"
  REM ***** electrostatic *****
    ELECF1(I) = -(KAPA * RIAP * Y(I))
    ELECF2(I) = EXP(ELECF1(I)) / (1 + EXP(ELECF1(I)))
    ELECF(I) = 4 * Pi * RIAP * 78.54 * 8.854E-12 * KAPA * ZETAP * ZETAB *
ELECF2(I) * .000001
    PRINT "Electrostatic force"; ELECF(I); "N"
  REM ***** hydrophobic *****
    HYD1 = ((1.6E-10) - (Y(I) * RIAP)) / 1E-09
    HYD2 = EXP(HYD1)
    HYD3 = (RIAP * RIAB) / (RIAP + RIAB)
    HYDFF(I) = 2 * Pi * HYD3 * G132 * HYD2
    PRINT "Hydrophobic force"; HYDFF(I); "N"
  REM ***** total forces *****
    TOTF(I) = VANF(I) + ELECF(I) + HYDFF(I)
    PRINT
    PRINT "Total force"; TOTF(I); "N"
RETURN
```

Appendix I

Micrographs



Figure I1 The sample of kaolin particles captured using scaning electron microscope, SEM.

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