COLLECTOR TRANSFER BETWEEN BUBBLE AND PARTICLE BY COLLISION

by

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M.Ed., University of Waikato, 2004 B.E. in Mineral Processing, Central South University, 1997

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF APPLIED SCIENCE

in

The Faculty of Graduate and Postdoctoral Studies

(Mining Engineering)

THE UNIVERSITY OF BRITISH COLUMBIA (Vancouver)

August 2016

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Abstract

The adsorption densities of dodecylamine hydrochloride at the quartz-liquid interface and at the bubble-liquid interface were measured in separate experiments using the solution depletion method. The amount of amine removed from solution by gas bubbles was measured by bubbling nitrogen through amine solutions of known concentrations and measuring the amount of amine remaining in solution. The obtained results were then compared with the amount of dodecylamine depleted from solution under flotation conditions when all three phases (solid, liquid, and gas) were present in the tested system. By analyzing the distribution of amine between the interfaces it was possible to identify the conditions (pH and amine concentration) leading to a transfer of amine between gas bubbles and quartz particles as a result of bubble-particle collisions.

Two modes of interaction between amine and quartz were identified. In a true solution system (pH 6), it was found that the surfactant could be transferred from gas bubbles to quartz particles only when the adsorption density of amine at the quartz-solution interface was relatively low, thus leaving space for additional amine adsorption, and the bubbles and the particles were oppositely charged in the presence of amine. Too high adsorption density, resulting in positively charged particles and bubbles largely prevented the amine transfer process. In a colloidal dispersion of amine (pH 11), the dynamic conditions of the flotation test actually seemed to lead to a lower amount of amine transferred to the froth zone than the theoretical amount calculated from adsorption on quartz and on gas bubbles. This result was attributed to the weak adhesion of the precipitate to the quartz particles as bubbles coalesced and burst in the froth zone. Interaction with quartz and bubbles was further weakened by the lack of electrostatic attraction between the nearly uncharged colloidal precipitate and the negatively charged bubbles and particles.

Experimental results supports the bubble transfer hypothesis (Digre and Sandvik, 1968) stating that under flotation conditions the adsorption of collector on solid surfaces is governed, to a large extent, by a transfer of collector from the gasliquid interface to the solid surface.

ii

Preface

This thesis is original, unpublished, independent work by the author, Haixing Yan.

Table of Contents

A	bstract		ii
Ρ	reface		iii
T	able of Co	ontents	iv
L	ist of Tab	les	vii
L	ist of Figu	ıres	viii
A	cknowled	Igements	x
1	Introdu	iction	1
	1.1 Imp	portance of this study	1
	1.2 Res	earch objectives	2
2	Literati	ure review	3
	2.1 Doc	decylamine Hydrochloride properties as a weak electrolyte collector	3
	2.1.1	Species distribution diagram of dodecylamine	3
	2.1.2	Critical micelle concentration (CMC)	5
	2.1.3	Domain diagram	7
	2.2 Sur	face properties of quartz	8
	2.2.1	Origin of surface charge	8
	2.2.2	Electrical double layer and Zeta potential	9
	2.3 Ads	sorption between solid, liquid and gas interfaces	12
	2.3.1	Amine adsorption on quartz in aqueous solution	12
	2.3.2	Adsorption at Liquid-Gas bubble interface	18
	2.3.3	Particle-Bubble attachment	19
3	Experi	mental program	23
	3.1 Ins	truments and materials	23
	3.1.1	Instruments	23
	3.1.2	Quartz	23
	3.1.3	Regents	25
	3.2 Me	thods	26
	3.2.1	i.e.p. of quartz	26
	3.2.2	Determination of slurry settling time	27
	3.2.3	i.e.p. of DAH precipitate measurement	29
	3.2.4	Adsorption method selection between shaker and bottle roll	29
	3.2.5	Adsorption Isotherm	31

	3.2.6	Adsorption tests without air	31	
	3.2.7	Bubbling tests	32	
	3.2.8	Adsorption tests with nitrogen	34	
	3.2.9	Total organic carbon analysis	36	
	3.2.10	Flotation	37	
4	Result	s and discussion	38	
4.	1 Det	ermination of testing conditions	38	
	4.1.1	i.e.p. measurement of quartz	38	
	4.1.2	i.e.p. of DAH precipitate	39	
	4.1.3	Setting time	39	
	4.1.4	Adsorption using Bottle roll and shaker	40	
	4.1.5	Adsorption isotherm of DAH on quartz	42	
	4.1.6	Bubbling test	43	
4.	2 Ads	sorption tests with and without nitrogen gas introduced	44	
	4.2.1	Adsorption tests at pH 6	46	
	4.2.2	Adsorption at pH 11	55	
5	Conclu	isions and future work	61	
Bib	liograp	hy		
Арр	endice	S	••	
Арр	endix 1	Calibration curves of DAH concentration versus TOC reading below 10	00	
	r	ng/l	68	
Арр	endix 2	Calibration curves of DAH concentration versus TOC reading below 10	00	
	-	400mg/l	69	
Арр	endix 3	TC calibration curve at concentration below 100 mg/l	70	
Арр	endix 4	TC calibration curve at concentration 100-400 mg/l	72	
Арр	endix 5	IC calibration curve at concentration below 10 mg/I	74	
Appendix 6: Particle size distribution of quartz				
Арр	endix 7	: Quantachrome autosorb automated gas sorption report	77	
Арр	endix 8	: Zeta potential of quartz at pH 2.0	78	
Арр	Appendix 9: Zeta potential of quartz at pH 3.079			
App	Appendix 10: Zeta potential of guartz at pH 4.0			
App	Appendix 11: Zeta potential of guartz at pH 6.7			
Ann	Appendix 12: Zeta potential of quartz at pH 9.0			
· •PP	5		5-	

Appendix 13: Zeta potential	of DAH (solid) precipitate at pH 10.898	33
Appendix 14: Zeta potential	of DAH (solid) precipitate at pH 10.948	34
Appendix 15: Zeta potential	of DAH (solid) precipitate at pH 10.978	35
Appendix 16: Zeta potential	of DAH precipitate at pH 10.768	36
Appendix 17: Zeta potential	of DAH precipitate at pH 10.878	37
Appendix 18: Zeta potential	of DAH precipitate at pH 10.968	38
Appendix 19: Zeta potential	of DAH precipitate at pH 10.978	39

List of Tables

Table 2.1 CMC measured by different methods	6
Table 3.1 Lane Mountain quartz sieve analysis results 2	23
Table 3.2 Chemical composites of Lane Mountain quartz	24
Table 4.1 Initial DAH concentration of 2 \times 10 ⁻⁴ M at pH 6 adsorption test result, fine	
quartz (BET specific surface area 0.15 m²/g)4	ŀ7
Table 4.2 Initial DAH concentration of 1.75×10^{-3} M at pH 6 adsorption test result,	
fine quartz (BET specific surface area 0.15 m²/g)4	18
Table 4.3 Initial DAH concentration of 2 \times 10 ⁻⁴ M at pH 11 adsorption test result, find	е
quartz (BET specific surface area 0.15 m²/g)5	56
Table 4.4 Initial DAH concentration of 1.75×10^{-3} M at pH 11 adsorption test result,	
fine quartz (BET specific surface area 0.15 m²/g)5	57

List of Figures

Figure 2.1	Dodecylamine species distribution diagram as a function of pH at total
	amine concentration 9 \times 10 $^{-5}$ M
Figure 2.2	Phase diagrams for aqueous DAH solutions at various pH
Figure 2.3	Domain diagram of aqueous solution of dodecylamine hydochloride7
Figure 2.4	Origin of surface charge of quartz9
Figure 2.5	Schematic representation of the electrical double layer in the vicinity of
	the solid-liquid interface11
Figure 2.6	Distribution of electrical potential in double layer surrounding a spherical
	charge particle11
Figure 2.7	Correlation between contact angle, adsorption density, zeta potential,
	and flotation recovery14
Figure 2.8	Adsorption isotherm of SDS on alumina at pH 6.5 showing a four-region
	isotherm
Figure 2.9	Effect of pH on quartz floatability in aqueous solutions of dedecylamine 18
Figure 2.1	0 Effect of pH on the potential of microbubbles generated in
	dodecylamine hydrochloride aqueous solution
Figure 2.1	1 Zones of interaction between a bubble and a particle
Figure 3.1	Davis Tube
Figure 3.2	ZetaView PMX100 Instrument
Figure 3.3	Bottle test and shaker
Figure 3.4	Adsorption results at DAH concentration of 2×10^{-4} M at natural pH (left)
	and pH 11 (right)32
Figure 3.5	Bubbling tests set-up
Figure 3.6	Heating the sample (left) to expel CO_2 , distilled water (right) as a
	reference for measuring temperature35
Figure 3.7	Shimadzu TOC-VCPH instrument (middle), ASI-V autosampler (left) and
	TOC-Control V software in computer (right)
Figure 4.1	i.e.p. of DAH precipitate at concentration of 2×10^{-4} M, inset of i.e.p. of
	quartz

Figure 4.2	Slurries turbidity after adsorption at pH=6 and pH=114	0
Figure 4.3	Adsorption tests using bottle roll method and shaker method4	1
Figure 4.4	Adsorption isotherm of DAH on quartz at pH 6 and pH 114	2
Figure 4.5	Percentage of total DAH removed from solution by bubbles at DAH	
	concentration of 1.75 × 10^{-3} M	3
Figure 4.6	Species distribution diagram of dodecylamine in aqueous at total	
	concentration of 2 × 10^{-4} M and 1.75 × 10^{-3}	9
Figure 4.7	Correlation of adsorption, contact angle, flotation response and zeta	
	potential for quartz as a function of dodecylammonium acetate	
	concentration at pH 6 to 7, 20 to 25 °C 4	9
Figure 4.8	Schematic representation of the physisorption of an aqueous cationic	
	surfactant on a negatively charged solid5	51
Figure 4.9	Colloidal precipitate aggregates at a DAH concentration of 2×10^{-4} M	
	(left) and 1.75 \times 10 ⁻³ M (right) at pH 11. Due to the lower density of solid	
	amine compared to the density of water, gradual accumulation of the	
	precipitate at the solution surface is clearly visible5	5
Figure 4.1	0 Effect of pH on electrophoretic mobility of microbubbles and quartz	
	particles in the presence of dodecylamine hydrochloride5	;9

Acknowledgements

Primary thanks must go to my supervisor, Dr. Marek Pawlik and co-supervisor Janusz Laskowski for the supervision of this research project. Also, I am most grateful to Dr. Maria Holuszko and Dr. Wenying Liu as my committee member for the advice on this project. Without their support this research would never have become a success.

In addition, I greatly appreciate the help of Mrs. Sally Finora, Mr. Pius Lo, who provided excellent assistance in the surface chemistry lab and the coal and mineral processing lab for accomplishing this research project. My thanks also go to Mrs Maria Lui, Mrs Leslie Nichols for the administrative support and other faculty members at the Norman B. Keevil Institute of Mining Engineering. To my colleagues Dr. Jophat Engwayu, Dr. Esau Arinaitwe, Dr. Libin Tong and other my friends, it's my honour to know you and thanks for your help in the school.

Finally, I also would like to dedicate this thesis to my family and thanks for their encouragements and supports to my research work.

1 Introduction

1.1 Importance of this study

It is well known that froth flotation is the most important mineral processing method by selective attachment of mineral particles to air bubbles to achieve specific separation from ores mixture. To achieve successful attachment in most cases, the improvement of hydrophobicity of mineral particles is required by collector adsorption on mineral surface. However, in quartz flotation, a good recovery can be achieved at very dilute dodecylamine concentration under normal flotation conditions. Digre and Sandvik (1968) proposed a hypothesis that adsorption of surface-active collectors on solid surface is governed, to a large extent, by a transfer of collector from the gas-liquid interface to the solid surfaces. The hypothesis is based on theoretical calculations, and the role of gas bubbles in transferring the collector has never been experimentally tested.

The Hallimond tube is a common small-scale lab flotation cell which can also be employed in adsorption tests because the air flow rate can be adjusted precisely with a flow meter installed. It is the research question of this thesis that by comparing the difference of the adsorption density of dodecylamine hydrochloride on quartz under aeration and without aeration, it should be possible to determine the amount of dodecylamine hydrochloride transferring between bubbles and the quartz surface as a result of bubble-particle collisions.

A series of preliminary studies were performed before adsorption tests were carried out for determining testing conditions and decreasing lab errors. Because the adsorption density of amine on quartz and bubbles at the tested concentrations of dodecylamine hydrochloride at neutral pH is extremely low, the detection of the small differences in the amounts adsorbed, with and without nitrogen gas, requires a very high reproducibility of the data with very small experimental errors. As a result, a significant part of the thesis is devoted to developing a reliable experimental procedure. To the author's knowledge, this research is the first study that amount of

1

collector transferred to quartz from bubbles during bubble-particle collision is determined in real flotation conditions.

1.2 Research objectives

To assess whether gas bubbles could transfer dodecylamine hydrochloride collector to the quartz surface by bubble-particle collisions, the following research objectives were formulated:

- 1) To develop an experimental procedure to measure the adsorption density of amine under flotation conditions.
- 2) To determine the distribution of amine between the quartz-solution, and gas-solution interfaces.
- 3) To determine the role of solution chemistry (pH) in the amine transfer process
- 4) To analyze the contribution of amine speciation to the transfer process in true solutions and in colloidal dispersions, or in the absence and presence of colloidal amine precipitates.

2 Literature review

2.1 Dodecylamine Hydrochloride properties as a weak electrolyte collector

2.1.1 Species distribution diagram of dodecylamine

Primary amines are weak bases. The electronegativity of amino nitrogen is caused by a single lone pair of electrons of amino nitrogen and polar covalent bonds of N-H, which build up additional negative charge around nitrogen atom. When a primary amine is dissolved in water, the lone electron pair of nitrogen can attract a hydrogen ion from water to form a coordinate bond. Because the primary amine donates its electron pair in this reaction, it behaves as a base according to Lewis Theory of acids and bases.

$$\mathsf{RNH}_{2(s)} \leftrightarrow \mathsf{RNH}_{2(aq)} \quad \mathsf{pK}=4.69 \text{ (Pugh, 1986)} \tag{2-1}$$

In aqueous solution, dodecylamine dissociation follows the reversible reaction 2-2.

$$RNH_3^+ \leftrightarrow RNH_2 + H^+ \tag{2-2}$$

When equilibrium for dodecylamine dissociation in aqueous solution is reached, the dissociation constant of dodecylamine K_a is expressed as

$$K_{a} = \frac{[C_{12}H_{25}NH_{2}]*[H^{+}]}{[C_{12}H_{25}NH_{3}^{+}]}$$
(2-3)

When dodecylamine is dissolved in aqueous solution, it has three forms of amine species in bulk solution: ionized amine (RNH_3^+), dissolved molecular amine (RNH_2), and solid precipitate of amine ($[RNH_2]_{precip}$). The total dodecylamine concentration ($[C_T]$) in bulk solution can be expressed by equation 2-4.

$$C_{T} = [RNH_{3}^{+}] + [RNH_{2}] + [RNH_{2}]_{precip.}$$
 (2-4)

At a specific pH, when ionic amine species concentration ($[RNH_3^+]$) is equal to molecular amine concentration ($[RNH_2]$) in bulk solution, the value of pKa is equal to this pH. At 25 0 C, pK_a for dodecylamine is 10.6 (Laskowski, 1989).

Since reaction 2-2 is reversible, the neutral species concentration of dodecylamine ([$C_{12}H_{25}NH_2$]) in aqueous solution, if it is below its solubility, changes with pH of solution. Therefore, by manipulating the pH of solution, a precipitate of dodecylamine can form when the neutral species concentration of dodecylamine exceeds its solubility limit. At 25 °C, the solubility (S) of undissociated dodecylamine in aqueous solution calculated according solubility equilibrium formula (2-1) is 2 × 10^{-5} M, which agreed with the value of (2.0 ± 0.2) × 10^{-5} M (Brown, 1958). By rearranging and combining equations 2-3 and 2-4, the pH of precipitation of dodecylamine (pH_{precip}) can be derived below.

$$pH_{\text{precip.}} = pKa + p(\frac{c_T}{s} - 1)$$
(2-5)

When dodecylamine dissolves in aqueous solution, concentrations of each dodecylamine species can be calculated based on equation 2-2 to 2-5

In dodecylamine solution, dodecylammonium ions may associate into dimers and ion-molecular complexes with dodecylamine molecules following reaction 2-6 and 2-7. Pugh (1986) constructed a dodecylamine species distribution diagram at dodecylamine concentration 9×10^{-5} M (Figure 2.1), which consisted of dodecylammonium ions, monomers and molecules solubilized, precipitated species and ion-molecular complexes in solution. It was shown that ion-molecular complexes achieved its maximum concentration at pH 10 near the pH where dodecylamine precipitate appeared. It was believed that ion-molecular complex was more surface active than the monomer

$$2RNH_3^+ \leftrightarrow (RNH_3^+)_2^{2+} \tag{2-6}$$

$$\mathsf{RNH}_3^+ + \mathsf{RNH}_2 \leftrightarrow (\mathsf{RNH}_2)_2 \mathsf{H}^+ \tag{2-7}$$



Figure 2.1 Dodecylamine species distribution diagram as a function of pH at total amine concentration 9×10^{-5} M (Pugh, 1986)

2.1.2 Critical micelle concentration (CMC)

The Krafft point is defined as the temperature at which the solubility versus temperature curve intersects the CMC versus temperature curve (Moroi, 1992, p115). For a surfactant with long hydrophobic chains dissolved in water, when the temperature is above its Krafft point, these surfactant molecules begin to rapidly aggregate into micelles in solutions. The appearance of micelles in solution will give rise to an abrupt change in solution properties such as viscosity, surface tension and specific conductivity (Bruce, 1990).

The CMC of solution can be measured according abrupt change in physical properties at Krafft point. Since there are differences in sensitivity and reliability of these methods, the reported CMC values of dodecylamine may be significantly different. Some CMC data of dodecylamine measured by different methods are listed in table 2.1.

Temperature, °C	CMC, M	Method	Author
25	1.46 × 10 ⁻²	Equivalent Conductance Graph	Brown et al.
25	1.47 × 10 ⁻²	Specific Conductance Graph	Ralston et al.
30	1.47 × 10 ⁻²	Density	Cart Aanac

Table 2.1 CMC measured by different methods (Mukerjee & Mysels, 1971)



Figure 2.2 Phase diagrams for aqueous DAH solutions at various pH (Dai & Laskowski, 1991)

For a weak electrolyte such as dodecylamine, its dissociation is influenced by pH of the bulk solution. Hence, the ratio of ionized molecules to nonionized molecules can be manipulated by adjusting pH of solution. When pH of solution changes, solubility and CMC of dodecylamine are affected correspondingly. Dai and Laskowski (1991) carried out a series of tests studying pH effect on the Krafft point and CMC of dodecylamine hydrochloride (DAH). The experimental results were plotted in Figure 2.2. They pointed out that the solubility and the CMC of

dodecylamine declined when pH increased, and the concentration range over which micelles appeared narrowed sharply with pH. At pH 10 and higher, the dissolved dodecylamine hydrochloride concentration was so low that micelles could not form. To distinguish from micelles, the dodecylamine precipitate was termed "precipitated colloidal particles"

2.1.3 Domain diagram

Dodecylamine as a weak electrolyte, its solubility depends on pH. In broad alkaline pH range, whenever the solubility limit is exceeded, a colloidal precipitate appears. To avoid solubility problems with dodecylamine in flotation, dodecylamine hydrochloride is commonly used to prepare a stock solution and then its pH is modified to a desired value. A domain diagram of dodecylamine hydrochloride, which showed zones of micellization and precipitation, was presented by Laskowski (1999) in Figure 2.3.



Figure 2.3 Domain diagram of aqueous solution of dodecylamine hydrochloride (Laskowski, 1999)

2.2 Surface properties of quartz

2.2.1 Origin of surface charge

When mineral particles are placed in water, the solid acquires electrostatic surface charges by different mechanisms.

For salt-type minerals, such as silver iodide (AgI), Calcite (CaCO₃), Silver sulfide (Ag₂S) etc., origin of surface charge can be explained by the lattice ion hydration theory. If the cation of solid surface has more negative hydration energy than the anion, the escaping tendency of the cation is larger than that of the anion, the solid surface will be negatively charged and vice versa. This phenomenon is called differential dissolution of constituent ions.

Potential determining ions (PDI) are species which by virtue of their electron distribution between the solid and liquid phase determine the difference in potential between these phases (Cosgrove & Ebrary, 2010). It is worth noting that constituent ions of a mineral are not always potential determining ions. When mineral particles are dissolved in water to some extent, the constituent ions may react with water to form other ions, which are not potential determining ions (PDI). These minerals are termed hydrolysable minerals, i.e. sulfides, phosphates and carbonates. For example, when a sulfide mineral is placed in aqueous solution in the presence of dissolved oxygen, the surface of the sulfide undergoes oxidation processes similar to electrolytic corrosion reactions (because sulfides are semi-conductors). S²⁻ ions may be oxidized to various species: S, S₂O₃²⁻ and S₂O₄²⁻. In this case, PDI is difficult to identify.

For oxide-type minerals, when they are placed in water, the surfaces easily become hydrated with water and form hydroxylated surfaces. The hydroxyl functional groups on mineral surfaces then dissociate or associate with H⁺ from aqueous solution and leave mineral surfaces charged. It is customarily believed that hydrogen and hydroxyl ions are potential determine ions for oxide minerals in aqueous solution, though there still remains a difference of opinion as to how pH controls the surface charge on oxide surfaces (Fuerstenau and Pradip, 2005). Therefore, the sign and magnitude of the surface charge of oxide-type minerals is pH dependent and can be adjusted by manipulating the pH of aqueous solution.

8

Quartz is a model oxide mineral to study surface properties of oxide. At 25 °C, the solubility of quartz in distilled water is 11 ± 1.1 mg/l (Rimstidt, 1997) resulting from the reversible reaction 2-8. When quartz is in contact with water, due to forming hydrophilic functional groups at the solid/liquid surface, the surfaces become strongly hydrophilic. The surface charge on the quartz surfaces originates from a two-stage process: forming functional groups (SiOH) and dissociation of functional groups. This process is depicted in Figure 2.4. As a result, there are three types of sites in equilibrium (positively-charged SiOH₂⁺, negatively-charged SiO⁻ and uncharged SiOH⁰ sites) and pH of aqueous solution plays a critical role in reactions 2-10 and 2-11.

$$SiO_2 + 2H_2O \leftrightarrow Si(OH)_{4 (aq)}$$
 (2-8)

$$SiO_2 + 2H_2O \leftrightarrow SiOH + 3OH^-$$
 (2-9)

$$SiOH + H^{+} \leftrightarrow SiOH_{2}^{+}$$
 (2-10)

and/or SiOH + OH⁻ \leftrightarrow SiO⁻ + H₂O (2-11)



Figure 2.4 Origin of surface charge of quartz

2.2.2 Electrical double layer and Zeta potential

When solid particles are immerged into aqueous solution, the particle surfaces are always charged electrostatically. There is always a charged layer coating on the particle surface, whose sign of net charge is opposite to the sign of particle surface charge and the magnitude of net charge is equal to the particle surface charge. This ion concentration profile around the particle is called the electrical double layer (EDL). Figure 2.5 (Birdi, 2008) clearly shows the Stern-Grahame model of electrical double layer in the vicinity of the solid-liquid interface. The adsorbed ions in the Stern plane constitute the compact layer, while loosely adsorbed ions outer the Stern plane constitutes the diffuse layer.

The plane that runs through the centers of weakly adsorbed hydrated counter-ions is called the outer Helmholtz plane. If ions adsorbed on the surface by specific adsorption, the plane that runs through the centers of such specifically adsorbed co-ions is called the inner Helmholtz plane. When the specific adsorbed ions are large organic ions, the inner Helmholtz plane could lie outside the outer Helmholtz plane (Fuerstenau et al., 2005). The inner Helmholtz plane and the outer Helmholtz plane form the Stern plane.

When a charged solid particle moves in aqueous solution, the plane where the relative movement takes place is called the shear plane. Inside the shear plane, the compacted Stern layer moves together with the particle, while the diffuse layer is sheared off. The potential at the shear plane is called the zeta potential (ζ). Because the distance between the Stern plane and the shear plane are very close, the potential difference between these two planes is small compared to the surface potential of the particle. It is customary to assume that the zeta potential is approximately equal to the potential of the Stern plane. Figure 2.6 depicts the surface potential decay.

When zeta potential is zero, the concentration of the potential determining ions is called the isoelectric point (i.e.p.). If there is no specific adsorption at the mineral-water interface, the net surface charge density of the mineral is equal to zero too.

There are four common types of electrokinetic phenomena: electro-osmosis, electrophoresis, streaming potential and sedimentation potential) (Fuerstenau et al., 2005). By far, the most commonly used to determine the zeta potential is electrophoresis. When particle is nonconducting and the radius of curvature of the

10



Figure 2.5 Schematic representation of the electrical double layer in the vicinity of the solid-liquid interface (Birdi, 2008)



Figure 2.6 Distribution of electrical potential in double layer surrounding a spherical charge particle (Birdi, 2008)

particle surface is much larger than the double-layer thickness, for the finely ground mineral particles in low solid content suspension, the Helmholtz-Smoluchowski equation (2-12) (Yoon & Kim, 1989) can be used to calculate zeta potential with measured electrophoretic motilities value.

$$\mu_e = \frac{\varepsilon \cdot \zeta}{4\pi\eta} \tag{2-12}$$

Where:

 μ_e : electrophoretic mobility, μ m/s/V/cm

 η : viscosity of the medium, Ns/m²

ε: dielectric constant of the medium

ζ: zeta potential, mV

For aqueous media with conductivity below 1 mS/cm, at 25 °C, the equation can be simplified to 2-13:

$$\zeta = 12.85\mu_e \tag{2-13}$$

2.3 Adsorption between solid, liquid and gas interfaces

2.3.1 Amine adsorption on quartz in aqueous solution

Adsorption at the liquid-solid interface can be classified into physical and chemical adsorption. For chemical adsorption, since there is a chemical bond forming between adsorbate molecules and adsorbent surface, the process involves a relatively higher energy change. This kind of adsorption is usually irreversible and form monolayer. For physical adsorption, it usually involves Van der Waals forces and electrostatic forces. The adsorption is characterized by a high rate of adsorption and forming of multilayers (Somasundaran & Krishnakumar, 1997).

The adsorption density expressed as Stern-Grahame equation (Fuerstenau et al., 2005), is commonly used to describe adsorption results.

$$\Gamma = 2rC \cdot exp(\frac{-\Delta G_{ads}}{RT})$$
(2-14)

Where Γ is the adsorption density in mol/cm², r is the effective radius of the adsorbed ions, C is the concentration of the bulk concentration in mol/cm³, ΔG^{0}_{ads} is the standard free energy of adsorption.

The standard free energy of adsorption is given by

$$\Delta G^{0}_{ads} = \Delta G^{0}_{elec} + \Delta G^{0}_{spec}$$
$$= \Delta G^{0}_{elec} + G^{0}_{chem} + \Delta G^{0}_{h} + \Delta G^{0}_{hpb} + \Delta G^{0}_{solv} + \Delta G^{0}_{hpb} * + \cdots$$
(2-15)

Where ΔG^{0}_{elec} is the change in standard free energy caused by electrostatic interaction, other terms represent changes due to chemical bonding, hydrogen bonding, hydrophobic bonding, and solvation effects. ΔG^{0}_{hpb} is resulting from surfactant chain interaction with a hydrophobic solid.

Amine adsorption onto quartz has been studied by many researchers over decades. A lot of tests were conducted at room temperature by changing either amine concentration or solution pH. Those studies attempted to elucidate the amine adsorption mechanism on quartz.

Fuerstenau (1957) plotted contact angle values from Gaudin and Morrow (1954, as cited in Fuerstenau 1957), adsorption density values from de Bruyn (1955, as cited in Fuerstenau 1957), zeta potential and flotation rate at a dodecylammonium acetate concentration of 4×10^{-5} M on one diagram to correlate solid-liquid interfacial phenomena (adsorption density and zeta potential) with solidliquid-gas interfacial phenomena (contact angle and flotation experiment) (See Figure 2.7). The adsorption process could be explained by an electrostatic adsorption model: cationic collector, which was ionized in aqueous solution and produced positively charged long chain amphiphiles, was supposed to adsorb on the negatively charged quartz surface with hydrophobic hydrocarbon "tails" extending into solution. With increasing pH up to around 8, the adsorption density increased only marginally even though the zeta potential of quartz increased towards more negative values. Once a sufficient amount of amine ions adsorbed at the interface, van der Waals attraction between hydrocarbon chains became effective and this phenomenon caused the increased adsorption of additional dodecylammonium ions at pH values higher than 8. Above pH 11, excess sodium ions displaced adsorbed dodecylammonium ions and zeta potential resumes the negative potential. Fuerstenau believed that dodecylammonium ions, not dodecylamine molecules act as the collecting agent.



Figure 2.7 Correlation between contact angle, adsorption density, zeta potential, and flotation recovery at dodecylammonium acetate concentration of 4×10^{-5} M (Fuerstenau, 1957)

The hemi-micelles hypothesis was proposed by Gaudin & Fuerstenau in 1955. In amine-quartz adsorption system, when the adsorbed dodecylammonium ions reached a concentration at the solid-liquid interface which was similar to the bulk CMC, the adsorbed ions associated into patches at the solid-liquid interface in the same way they associated to micelles in the bulk solution. These patches were called hemi-micelle.

Smith (1963) suggested that both dodecylamine ions and the dodecylamine molecules were active species in a quartz-dodecylamine solution-nitrogen gas system and coadsorption of amine ions and amine molecules took place on quartz. At low pH, where amine cations dominated, adsorption was through electrostatic attraction between the positively charged amine ions and the negatively charged

quartz surface, though there was a strong lateral repulsion between the adsorbed individual amine ions on the quartz surface. At high pH, there were neutral amine molecules existing in bulk solution in addition to a sufficient quantity of amine ions. These molecules could be adsorbed onto the quartz by capture by dodecylamine ions, or, more probably, by dodecylamine hemimicelles. The function of neutral molecules in adsorption was to screen or lower lateral electrostatic repulsion between adsorbed amine ions. So the hydrophobicity of quartz was improved resulting from increased adsorption density by coadsorption of ions and molecules. The results showed that contact angle increased from a maximum of 36°C, when amine ions were mainly present, to a maximum of 86°C when both amine ions and neutral molecules were present in sufficient quantities.

The classical Somasundaran-Fuerstenau (1966), isotherm with four characteristic regions was often used to explain the mode of surfactant adsorption on an oppositely charged surface, as illustrated in Figure 2.8 for the adsorption of sodium dodecyl sulfate (SDS) on alumina. The model (Somasundaran & Krishnakumar, 1997) had four regions corresponding to four adsorption mechanisms with increasing SDS concentration at neutral pH 6.5. It should also be noted that alumina was positively charged at pH 6.5 since the i.e.p. of alumina was at pH 9. In Region I, at low surfactant concentrations, the surfactant ions were adsorbed individually onto the solid surface through electrostatic interactions between the ionic surfactant and the oppositely charged solid surface. In Region II, adsorption was characterized by a marked increase in the adsorption density, which was attributed to the onset of formation of hemimicelles through lateral attractive interactions between hydrocarbon chains. In Region III, the adsorption was marked by a decrease in the slope of the isotherm, which was ascribed to the increasing hindrance to surfactant adsorption caused by the adsorption of charged species. The i.e.p. corresponded the transition point from Regine II to Regine III. In Region IV, the isotherm reached maximum adsorption density, which was due to micelle formation and monolayer coverage.



Figure 2.8 Adsorption isotherm of SDS on alumina at pH 6.5 showing a fourregion isotherm (Zhang & Somasundaran, 2006)

As shown in Figure 2.1, when the pH of solution increased above about 5.7, undissocciated amine molecule appeared in solution, following formation of amine/ammonium complex ($RNH_2RNH_3^+$). Kung and Goddard (1969) revealed that the conversion of individual species to a complex form was complete when equimolar amounts of amine molecules and ions were mixed together and an ion-molecule was a 1:1 amine-ammonium complex that was highly stable.

The formation of ion-molecules complexes played an important role in rendering the mineral surface hydrophobic. The results showed that the flotation of quartz with dodecylamine hydrochloride was very efficient over the concentration and pH range in which ion-molecular complexes predominated (Laskowski, 1989). Somasundaran (1976) suggested that complex formation increased flotation because the surface activity of ion-molecular complexes was significantly higher than the surface activities of the individual complex-forming species. The

16

mechanism of adsorption of ion-molecular complex was assumed to be similar to that of the electrostatic adsorption of cationic surfactant on the negatively charged mineral surface. The results of Puph (1986) results suggested that though the amine/ammonium complex was present at a relatively low concentration of 2.2 mol%, because of their high surface activity, the formation of ion-molecular complexes in solution could promote a synergistic co-operation process involving several types of pre-micelle species leading to the formation of an hydrophobic mixed hemi-micelle structure at the mineral surface, which consisted of ion-molecular complexes, together with dimers, monomers and molecular solubilized and precipitated species.

Castro, Vurdela and Laskowski (1986) investigated the associative interactions among ionizable and molecular species of dodecylamine in alkaline solutions. Precipitation was induced either by increasing the pH or the surfactant concentration. When pH approached the pH of precipitation, premicellar association of neutral molecules had been suggested. The precipitation reaction started with the formation of a dimer composed of two neutral molecules, then dimers associated to form larger polyassociations, culminating in the formation of insoluble colloidal aggregate. The dodecylamine colloidal precipitate exhibited an isoelectric point at about pH 11.

Quartz flotation tests using dodecylamine in the alkaline pH range were carried out by Laskowski, Vurdela and liu in 1988 (as cited in Laskowski, 1989). The results shown in Figure 2.9 indicated that the recovery was excellent over the pH range from 9 to 11 when dodecylamine concentration was below its solubility limit. But the flotation of quartz was depressed over this range when dodecylamine concentration exceeded the solubility limit. They concluded that the excellent flotation behavior at dodecylamine concentration below solubility limit was due to the presence of ion-molecular complexes. The depression effect, when the dodecylamine solubility limit was exceeded and the reagent formed a precipitate, was because both quartz and gas bubbles coated with the dodecylamine precipitate acquired almost identical electrokinetic potentials.



Figure 2.9 Effect of pH on quartz floatability in aqueous solutions of dodecylamine (Laskowski, et al., 1988)

2.3.2 Adsorption at Liquid-Gas bubble interface

Laskowski, Yordan and Yoon (1989) investigated the electrokinetic potentials of microbubbles generated in aqueous solution of dodecylamine hydrochloride using the microelectrophoretic technique. It was found that isoelectric points of bubbles were a function of pH, either positive or negative. In distilled water in the absence of any of surfactants, the i.e.p.s of bubbles were reported at pH 4.85 by EKserova and Zakharieva (1975, as cited in Laskowski et al., 1989) and pH 4.5 by Takahashi (2005). The isoelectric points of bubbles were consistently very close to the isoelectric points of the colloidal precipitate present in the solution when the solubility limit of dodecylamine hydrochloride was exceeded. This suggested that the dodecylamine precipitate coated the bubbles and rendered the zeta potential of the bubbles close to that of the precipitate itself. So the negative sign of the zeta

potential of bubbles produced in alkaline aqueous solution was explained by armoring of bubbles by the partially hydrophobic dodecylamine hydrochloride precipitate.



Figure 2.10 Effect of pH on the potential of microbubbles generated in dodecylamine hydrochloride aqueous solution (Laskowski et al., 1989).

As shown in Figure 2.10, at dodecylamine hydrochloride concentration of 1×10^{-4} M, the isoelectric points for bubbles was around pH 9.1, which was lower than the pH of precipitation for the bulk solution at the same surfactant concentration. This indicated that at the liquid-gas interface amine precipitation took place before precipitation in bulk solution.

2.3.3 Particle-Bubble attachment

To separate hydrophobic particles from hydrophilic particles by flotation, selective attachment of a hydrophobic particle to an air bubble was the key factor

controlling the flotation process. For a successful attachment, three stages were of critical importance (Leja, 1982, p578):

- 1. The thinning of the intervening liquid layer separating the particle and the air bubble
- 2. The rupture of the thinning layer to its black film thickness followed by establishment of a bound particle-bubble
- 3. The withdrawal of water, receding from the black film, thus expanding the hole



Figure 2.11 Zones of interaction between a bubble and a particle (Derjaguin and Dukhin, 1961)

Derjaguin and Dukhin (1961) divided the process of the particle-to-bubble attachment into three zones shown in Figure 2.11. In zone 1, the particle passed through it under the action gravity and inertia. The hydrodynamic forces operated without contribution from surface forces. Zone 2 was called a diffuso-phoretic zone where the diffusion acts and electrophoretic potential was created due to the concentration gradient of ionic surfactant and the differ of cation and anionic diffusion coefficients in this zone. In zone 3, the electrical double-layer and van der

Waals forces was dominant independent of whether the bubble was at rest or in motion. All these forces in zone 3 defined the magnitude of a force barrier against the rupture and out of collisions between bubbles and particles. The energy barrier was a primary obstacle for attachment. For the attachment to be possible, the particle and bubble must first overcome the energy barrier (Laskowski, Xu, Yoon, 1991), which included the electrostatic, dispersion and hydrophobic interaction energies (Roe-Hoan and Laiqun, 1996).

Ralston, Fornasiero and Hayes (1999) defined the capture efficiency E of a bubble and a particle as:

 $E = E_c \cdot E_a \cdot E_s \tag{2-16}$

Where E_c was the collision efficiency, E_a is the attachment efficiency and E_s was the stability of the bubble-particle aggregate.

Schulman and Leja (1954, 1958 as cited in Leja, 1982, p.589) believed that the attachment of predominantly collector-coated particles to predominantly frothercoated air bubbles occurred as a result of penetration of two interfaces to form a solid/ gas interface, possessing a higher density of surfactant coverage than either the gas/liquid or liquid/gas interface.

2.4 Collector transfer from bubble to particle

Digre and Sandvik (1968) suggested that collector adsorption measured at the liquid-mineral interface before introduction of air bubbles could not represent the actual adsorption amount during flotation because such low collector coverage of the mineral surface should not give good flotation. They formulated the bubble transfer hypothesis without directly measuring adsorption densities at solid-gas interface and solid-liquid interface. When the ground minerals were exposed to a dilute collector solution, both mineral and bubble surfaces adsorbed the collector. By collision between a bubble and a mineral grain, the collector was transferred from the bubble to the mineral surface, which was rendered more hydrophobic. For the particles, which were not hydrophobic enough to attach themselves to bubbles, the process would be repeated until collector coverage was sufficient for attachment to bubbles. Pope and Sutton (1971) investigated the validity of Digre and Sanvik's hypothesis by measuring the extent of adsorption of oleate on ferric oxide before and after flotation using differential thermal analysis. The adsorption isotherms showed that the extent of adsorbed collector on the floated fractions never exceeded that on the conditioned but unfloated material. The reason was that the affinity of the gas bubble/liquid interface for collector ions leads to the removal of some of the adsorbed oleate from the less favoured sites on the oxide surface. It was concluded that when an oxide was conditioned under adsorption equilibrium, the floated material did not show a greater collector adsorption than a similar, unfloated material. This find was contrary to Digre and Sanvik's hypothesis.

Finch and Smith (1975) exploited the time-dependent surface tension of alkaline dodecylamine acetate solutions and correlated the surface tension with the tenacity of bubble-solid attachment by performing captive bubble, bubble pick-up and flotation tests. The results showed that the tenacity of bubble-solid attachment decreased with decreasing bubbles surface tension for a variety of solids (magnetite, hematite, quartz, glass and Teflon). The presented evidence did not support the bubble transfer model of flotation.

Fuerstenau (2001) carried out experiments using a Pyrex disk and aqueous dodecylammonium acetate films, and showed that the velocity of the receding film increased markedly if the tests were repeated at short time intervals. In the modified Hallimond tube tests, reflotation of particles after bubbles had been removed showed an increase in flotation rate. The results indicated that collector could be transferred from bubbles to particles under non-equilibrium adsorption conditions and thus could enhance flotation.

22

3 Experimental program

3.1 Instruments and materials

3.1.1 Instruments

The Shimadzu TOC-V_{CPH} total organic carbon analyzer was used for measuring the organic carbon concentration in solution, which was calibrated with respect to the concentration of DAH. In adsorption tests without air, an IKA KS 4000 ic control shaker and a bottle roller were used for mixing quartz slurry at ambient temperature. To get rid of magnetic impurities in the quartz sample and obtain the narrow size fraction of quartz, a Davis Tube Tester for purifying quartz, a Ro-Tap and Gilson U.S.A Standard test sieves for sizing were employed in sample preparation. Malvern Mastersizer 2000 was employed to measure the particle size distribution of quartz samples used for adsorption tests. To centrifuge suspension slurries and to separate the solids from the liquid, a Heraeus Biofuge Primo centrifuge was employed in this study. A Quantachrome Autosorb-1MP BET analyzer was used for determining the specific surface area of the quartz samples. The zeta potentials of the quartz particles were measured by ZetaView PMX100.

3.1.2 Quartz

The quartz used in the study was Lane Mountain Silica Sand LM#70, which was 22.7 kg per bag. The sieve analysis results given by the company were shown in Table 3.1.

U.S sieve	Metric size, µm	Size of LM#70, %
No. 40	425	0
No. 50	300	0-5
No. 70	212	20-45
No. 100	150	20-45
No. 140	103	10-25
No. 200	75	5-15
Bala	0-10	

 Table 3.1 Lane Mountain quartz sieve analysis results

Composites	Content, % wt.
Silicate, SiO ₂	99.56
Aluminum Oxide, Al ₂ O ₃	0.24
Iron Oxide, Fe ₂ O ₃	0.042
Calcium Oxide, CaO	0.0051
Magnesium Oxide, MgO	0.0079
Titanium Dixoide, TiO ₂	0.016
Loss on Ignition at 1180 °C	0.13

The chemical analysis provided by the company was listed below in Table 3.2:

Table 3.2 Chemical composites of Lane Mountain quartz



Figure 3.1 Davis Tube

The particle size of this sample appeared to be coarse for flotation. In order to get the quartz sample with a particle size distribution more amenable for flotation and shorter settling time after adsorption in order to decrease experimental error, the

sample was dry-screened using US standard sieves on a Ro-tap sieve shaker and the -105+38 micron size fraction of quartz was extracted.

To purify the sample, the quartz sample was processed by a Davis Magnetic Tube. The sample was flushed slowly down through the strong magnetic field in the cylindrical glass tube by deionized water. The non-magnetic quartz was flushed to a container while magnetic impurities were strapped in the glass tube (see Figure 3.1). The cleaned quartz pulp sample was rinsed on a 38 µm sieve (400 mesh) using deionized water and dried, then stored in a sealed glass bottle. The underflow of the sieve was collected for zeta potential measurements.

The particle size distribution of quartz sample was measured using Malvern Mastersizer 2000. The volume mean diameter of the sample was found to be 70.5 microns with a top size ~105 microns. The size fraction below 40 microns was 3.5% and the fraction above 112 microns was 4.0%. The cumulative volume particle size distribution curve can be found in Appendix 6.

The specific surface area of quartz was determined by a Quantachrome Autosorb-1 MP BET (Brunauer Emmett Teller) analyzer using nitrogen as adsorbate. The surface area was found to be $0.15 \text{ m}^2/\text{g}$ for the quartz sample in the -105+38 micron size fraction.

3.1.3 Reagents

Sodium chloride from Fisher Scientific with 99.8% purity was used in adsorption tests as background electrolyte solution. To prepare a 5×10^{-3} M NaCl background solution, 292.8 mg NaCl was weighed in a 50 ml beaker on an analytical balance. The NaCl was transferred to a 1 liter volumetric flask by flushing the beaker with several small volumes of distilled water. Distilled water was then added to the 1 liter mark and a stir bar was placed into the flask. The volumetric flask was put on a magnetic stirrer for mixing the solution for 1 hour before used in tests.

1-Dodecylamine hydrochloride with 97% purity from Alfa Aesar was used as adsorbate in adsorption tests. To prepare a 3.5×10^{-3} M DAH solution, 800.3 mg DAH power was weighed in a 50 ml beaker on an analytical balance and then it was transferred to a 1 liter volumetric flask by flushing the beaker with a sufficient

25

amount of distilled water. The volumetric flask was swirled gently for 3 minutes to partly dissolve DAH solid in order to decrease error. The volumetric flask was made up to 1 liter mark using distilled water. A stir bar was placed into the volumetric flask. The solution was mixed for 5 hours on a magnetic stirrer before being used for tests. All the DAH solutions at different concentrations were prepared following the same procedure.

For adjusting pH, hydrochloric acid (HCI) and sodium hydroxide (NaOH) solutions with different concentration were made. Concentrated HCI solution from Fisher Scientific Company was diluted with distilled water into 2 M, 1 M and 0.5 M HCI solutions. NaOH (pellets) from Fisher Scientific Company was weighed and dissolved in distilled water to prepare 2 M, 1 M and 0.5 M NaOH solutions.

3.2 Methods

3.2.1 i.e.p. of quartz



Figure 3.2 ZetaView PMX100 Instrument

The i.e.p. of the quartz sample was measured using the ZetaView instrument shown in Figure 3.2. It consists of a cell unit, a laser, a microscopical imaging unit with video camera, and two motorized carriages. When laser light illuminates
particles in aqueous solution, they reflect light. The image of the scattered light is focused onto the video camera. Upper and lower measurement limits depend on the material being measured, the upper limit being migration determined by migration of particles, the lower limit being the scattering efficiency of the particles. Particles between 100 nm and10 µm can be measured. The approved pH range for the cell is between 2 to12.

The cell is negatively charged. When an electric field is applied to the cell, it causes the liquid to flow into one direction at the cell walls and in the middle of the cell the liquid carrying the particles flows to the opposite direction. From measuring the particle velocity between the "negative" and the "positive" flow domains, a plane can be located where the electro-osmosis velocity is zero, named "stationary layer", and the Zeta potential of particles can be determined by Smoluchowski equation.

To determine the i.e.p. of the quartz sample, 100 ml of slurry containing the -38 micron quartz size fraction was measured into a 250 ml beaker. The pH of the quartz slurry was adjusted to 2 using HCl solution. The cell of the ZetaView was flushed with distilled water first, and then it was flushed with the quartz slurry. The waiting time before the start of zeta potential measurement was 15 minutes.

The zeta potential of quartz was measured using the underflow quartz slurry at pH 2, 3, 4, 6.6 and 9. Then the zeta potential of quartz versus pH curve was plotted and the pH of the point of intersection on the pH axis was the i.e.p. of the quartz sample.

3.2.2 Determination of slurry settling time

Before sampling supernatant solution for TOC measurement, the solid quartz in the residue slurry after adsorption requires to be removed by means of filtration or centrifuging or settling. To decrease experimental error, this process should be completed in a minimal time, because DAH adsorption on quartz continues during the process. The settling method was selected to meet this requirement based on preliminary tests and analysis.

The Hach Model 2100AN Laboratory Turbidimeter can measure turbidity from 0 to 10000 NTU (Nephelometric Turbidity Units). The optical system of the

Turbidimeter is comprised of a tungsten-filament lamp, lenses and apertures to focus the light, a 90° detector to monitor scattered light, a forward-scatter light detector, a transmitted-light detector, and a back-scatter light detector. When the ratio mode is on, the instrument uses the complete set of detectors, which have benefits of excellent linearity, calibration stability, wide measurement range, and the ability to measure turbidity in the presence of color. In this research, the measurement is made with automatic range selection, Ratio and Signal Average on.

To determine the time of settling slurry after adsorption in order to take sample for total organic carbon measurement, a group of turbidity tests had been carried out.

5 g quartz was weighed into a Nalgene bottle on an analytical balance before 25 ml 5 \times 10⁻³ M NaCl solution was added into this bottle. The bottle then was placed on an IKA shaker mixing 15 minutes at 220 rpm. 25 ml 4 \times 10⁻⁴ M DAH was measured using a 25 ml volumetric pipette and was placed into the bottle, after which the bottle was shaken for 30 minutes on the table shaker at 220 rpm.

After adsorption at natural pH, the slurry was shaken and poured into a 30 ml sample cell for turbidity measurement by HACH 2100AN Turbidimeter.

For turbidity test after adsorption at pH=11, 5g of quartz was weighed into a 125 ml Nalgene bottle on an analytical balance and then 25 ml 5×10^{-3} M NaCl solution was transferred to the bottle. The bottle was shaken for 15 minutes at 220 rpm on the table shaker before the pH was adjusted to 11. 25 ml 4 × 10^{-4} M DAH was measured into a 50 ml beaker using a volumetric pipette and the pH was adjusted to 11. The DAH solution was poured into the Nalgene bottle and the mixed slurry was shaken for 30 minutes on the shaker at 220 rpm. After adsorption at pH=11, the slurry was poured into a 30 ml sample cell for turbidity measurement.

The turbidity of the adsorption slurry versus settling time was plotted and the settling time before taking a sample for TOC measurement without significant quartz left in the solution was determined.

3.2.3 i.e.p. of DAH precipitate measurement

To determine i.e.p. of DAH precipitate, zeta potential of DAH solutions at different pH values were measured using ZetaView instrument.

1 liter of 2 \times 10⁻⁴ M DAH with 2.5 \times 10⁻³ M NaCl background electrolyte solution was prepared by weighing 45.7 mg of DAH and 146.8 mg of NaCl crystals. 150 ml of the stock solution was poured into a 250 ml beaker and its pH was adjusted to around 10.7 by adding NaOH solution. In this way, amine precipitation was induced by high pH. After the cell of ZetaView was flushed first with distilled water and then with the sample solution, a representative DAH precipitate sample was taken and injected into the ZetaView sample cell for zeta potential measurement.

Another way of introducing amine precipitation was add DAH solid into solution at pH 11. 1 liter of NaCl solution at concentration 2.5×10^{-3} M was prepared first using a 1 liter volumetric flask. 150 ml NaCl solution was poured into a 250 ml beaker and its pH was adjusted to about 10.9. After add 6.9 mg DAH solid into the beaker to make 2 × 10⁻⁴ M DAH solution, the solution was mixed for 5 hour with a stir bar on a magnetic-stirrer device. The zeta potential of the DAH precipitate was measured.

A set of zeta potential tests in the pH range from 10.7 to 11 were performed and the zeta potential of DAH precipitate versus pH was plotted. The pH of the point of intersection on pH axis was i.e.p. of DAH precipitate.

3.2.4 Adsorption method selection between shaker and bottle roll

The amount of DAH adsorbed onto quartz surface can be measured by depletion of DAH in solution.

$$\Gamma = \frac{(Cin-Ceq) \times V}{M_q \times S_{BET}}$$
(3-1)

Where:

 Γ - adsorption density, mg/m²

Cin - initial concentration of DAH in suspension, mg/l

Ceq - equilibrium concentration of DAH after adsorption, mg/l

V - slurry volume, I

M_q - mass of quartz, g

 S_{BET} - specific surface area of quartz measured by BET, m²/g

A series of preliminary adsorption tests were carried out to determine the DAH adsorption curve at varying pH values. There was a concern that precipitated aggregates of DAH may mechanically be trapped in the quartz bed after vigorously shaking on the shaker, because it was observed that colloidal precipitate could aggregate into large aggregates during the shaking process. This phenomenon would result in overestimation of the adsorbed amount. Therefore the preliminary adsorption tests were performed following two methods: table shaker test and bottle roll test.





For a table shaker test, 3 g quartz was weighed into a Nalgene bottle on an analytical balance, followed by 25 ml of 5×10^{-3} M NaCl solution into the bottle. After the bottle was placed on the shaker, the sample was mixed for 15 minutes at 220 rpm, and then the slurry pH was adjusted to a desired pH value using NaOH and HCl solutions. 25 ml of 4 × 10^{-4} M DAH solution was measured using a 25 ml volumetric pipette into a 50 ml beaker, followed by adjusting the pH to the same value as the slurry pH was measured again. The Nalgene bottle was placed on the shaker, shaken for 30 minutes at 220 rpm, followed by standing for 5 minutes. An

aliquot of the 25 ml sample solution was taken using a 10 ml syringe and placed into a 40 ml ASI-V autosampler vial. The sample pH was modified to around 2.7 by adding HCl solution, before it was heated to 35 °C on a hot plate to expel CO₂. After the sample solution was cooled down to room temperature, it was transferred to the TOC autosampler for the TOC measurement.

For bottle roll method adsorption, the procedure was same as for the table shaker method except that the Nalgene bottle was placed inside a larger bottle which in turn was put onto a bottle roller. The roller was gently run at 3 rpm for 30 minutes.

A series of adsorption tests were performed using these two methods at different pH values from 6 to 11.5.

3.2.5 Adsorption Isotherm

To determine the DAH concentration which would be employed in following tests, several adsorptions tests without air were performed at varying DAH concentrations at natural pH and pH 11 using the shaker method determined by preliminary tests. The adsorption tests followed the same procedure as described in section of 3.2.4 for the shaker method. The adsorption tests carried out in the concentration range from 4×10^{-5} M to 5.12×10^{-3} M. As shown in Figure 4.7 (Fuerstenau, 1964), this DAH concentration range covered almost all the DAH concentrations for quartz flotation. The quartz flotation response experienced from below 10% to above 80%. The adsorption density result was then plotted as function of initial DAH concentrate.

3.2.6 Adsorption tests without air

Adsorption tests without nitrogen gas introduced were carried out at concentrations of 2×10^{-4} M and 1.75×10^{-3} M with NaCl background electrolyte at 2.5×10^{-3} M at natural pH and pH 11 in Nalgene bottles using the shaker method. The tests followed the procedure of shaker method in 3.2.4, except using 5g quartz as adsorbent.



Figure 3.4 Adsorption results at DAH concentration of 2×10^{-4} M at natural pH (left) and pH 11 (right)

Figure 3.4 show comparison of adsorption results after setting 1 minute at DAH concentration of 2×10^{-4} M at natural pH and pH 11. As shown in the left picture, there is a layer of quartz floated on the top of solution after adsorption test at natural pH, while at pH 11 there is almost no quartz floated on the top of the solution after adsorption. It seemed DAH collector rendered quartz at natural pH more hydrophobic than at pH 11.

3.2.7 Bubbling tests

To determine the DAH adsorption amount on bubbles when nitrogen gas was introduced into the quartz flotation system, the adsorption tests without quartz at DAH concentration of 2×10^{-4} M and 1.75×10^{-3} M at neutral pH and pH 11 were performed.

1 liter of 1.75×10^{-3} M DAH solution and 1 liter of 2×10^{-4} M DAH solution both with 2.5×10^{-3} M NaCl background electrolyte were prepared following procedure in reagent section in 3.2.1. The experiment set-up in Figure 3.5 shows bubbling test at DAH concentration of 1.75×10^{-3} M at pH 11. 200 ml of the stock DAH solution was poured into a 250 ml beaker. 50 ml DAH solution was measured using a 50 ml volumetric pipette, which was rinsed 4 times with stock solution before measurement, into a modified Hallimond tube. The pH of the solution in the Hallimond tube was adjusted to desired value using HCl and NaOH solutions. Afterwards, the Hallimond tube fixed by a clamp stand was put on a magnetic stirrer. When compressed

nitrogen gas was introduced, timing was started. Once the pre-set bubbling time was reached, nitrogen gas was cut off by releasing the clamp (Figure 3.5). It was observed that a large volume of stable foam formed as a result of bubbling nitrogen through the amine solutions. As a result, a 25 ml sample of the bulk solution was taken as quickly as possible using a 10 ml syringe and transferred to a vial for TOC analysis. The pH of the sample solution in the vial was adjusted to around 2.7 by adding HCl solution and then heated up to 35°C to expel dissolved CO₂. The sample was cooled down to room temperature for TOC measurement.



Figure 3.5 Bubbling tests set-up

Bubbling tests were performed for 1.75X10⁻³ M DAH solution at 30 seconds, 60 seconds and 120 seconds, and for 2X10⁻⁴ M DAH solution at 30 seconds using a nitrogen flow rate of 100 ml/min, at natural pH and pH 11. Each test was done three times to assess repeatability. During all bubbling tests, the same Hallimond tube was used to reduce errors.

3.2.8 Adsorption tests with nitrogen

Adsorption tests with nitrogen were carried out at natural pH and pH11 in a Hallimond tube.

5 g of quartz was weighed into a 50 ml beaker on an analytical balance, followed by 25 ml of 5×10^{-3} M NaCl solution into the beaker. After a small magnetic stir was put in the beaker, the beaker was sealed with Parafilm. The slurry was mixed for 15 minutes on a magnetic stirrer at room temperature, and then the slurry pH was modified to the desired value using NaOH and HCl solutions. Afterwards, 25 ml of 4×10^{-4} M DAH was measured using a 25 ml volumetric pipette into the bottom part of Hallimond tube, followed by adjusting pH to the desired value. The quartz slurry together with the magnetic stir in the beaker was then poured into the Hallimond tube, which was fixed on a clamp stand above a magnetic stirrer. To decrease errors, the amounts of addition of acid or base were determined prior to adsorption tests in preliminary tests.

The pulp was conditioned for 2 minutes with a small stir bar running on the bottom of the Hallimond tube. Once compressed nitrogen was introduced into the slurry, the flotation commenced. The nitrogen flow rate was carefully maintained at 100 ml per minute during all adsorption tests in the presence of gas bubbles.

The flotation time was controlled at 30 seconds. For flotation test at natural pH, when the flotation stopped, there was almost no quartz left at the bottom in the Hallimond tube. While for flotation test at pH 11, there was a significant amount of quartz left at the bottom of the Hallimond tube. Even if the flotation time at pH 11 was increased to 150 seconds, quartz on the bottom could still not be floated. It was clear that flotation of quartz with amine at pH 11 was very difficult.

After flotation was ceased, compressed nitrogen was shut off by releasing the clamp of a three-way connector. After the slurry was allowed to stand for 60 seconds, no quartz particles could be seen suspended in the pulp. A 25 ml sample solution was taken using a 10 ml syringe into a 40 ml ASI-V vial as quickly as possible.



Figure 3.6 Heating the sample (left) to expel CO₂, distilled water (right) as a reference for measuring temperature

The pH of sample solution was adjusted to around 2.7 by adding 2 M HCl solution and then heated up to 35°C to expel dissolved CO₂. The volume of HCl addition for pH modification has been determined in preliminary tests. When the sample solution was heated, another vial, which was filled with 25 ml distilled water at room temperature, was placed on the heater next to the sample vial. Temperature of the sample vial was determined by reading of distilled water vial, in order to avoid contaminating sample solution by the thermometer (see Figure 3.6).Then the sample vial was sealed with a lid and cooled down to room temperature for TOC measurement.

The adsorption tests conditioned 2 minutes without compressed nitrogen introduced into the Hallimond tube were also performed.

All adsorption tests were repeated at least three times.

3.2.9 Total organic carbon analysis



Figure 3.7 Shimadzu TOC-VCPH instrument (middle), ASI-V autosampler (left) and TOC-Control V software in computer (right)

The Shimadzu TOC-V_{CPH} is used to analyze the total organic carbon contained in water samples. It adopted "Oxidative combustion-infrared analysis" method to measure the amount of total carbon (TC), inorganic carbon (IC) and total organic carbon (TOC) in water. If high sensitivity analysis kit is installed, the instrument is capable of detect trace amounts (commonly 0.5 mg/l or less) of TOC in samples.

After a sample introduced into the TOC analyzer is burned in a combustion tube, the combustion product is brought by carrier gas passing through dehumidifier, halogen scrubber to the cell of a non-dispersive infrared (NDIR) gas analyzer, where the carbon dioxide is detected. The NDIR outputs analog signal that forms a peak and the peak is measured by TOC-Control V software. The area under the peaks can be calibrated using amine solutions of known concentrations. The calibration curves for standard amine solutions are listed in the appendix 1 and appendix 2. TOC can be measured using 3 methods: TC-IC method, NPOC (Non-Purgeable Organic Carbon) method and POC (Purgeable organic carbon)+NPOC method. In preliminary tests, it was noticed that samples used in this research met the TC-IC method requirement: non-purgeable sample, IC below 10ppm and TOC greater than IC. Therefore, the TC-IC method was used for determining the TOC in samples for all the tests.

To decrease errors from IC (including carbonate and dissolved carbon dioxide) in the samples, samples were acidified with a small amount of hydrochloric acid to reach a pH of 2.5 to 3 to convert all carbonates to carbon dioxide. Then the water samples were heated to 35 °C on a heater to drive off dissolved carbon dioxide from the samples. The samples were placed in 40 ml ASI-V vials and cooled down to room temperature before TOC measurement.

3.2.10 Flotation

The Hallimond tube flotation tests at DAH concentrations of 2×10^{-4} M and 1.75×10^{-3} M with 2.5×10^{-3} M background electrolyte at natural pH and pH 11 were performed to assess the effect of adsorption amount with nitrogen introduced on flotation recovery under changing concentrations of DAH and pH conditions.

The slurry of 5g quartz and 65 ml NaCl solution were mixed in a 200 ml beaker for 15 minutes. After 65 ml DAH solution was measured into the same beaker, the slurry was conditioned for 2 minutes. Then the slurry was transferred to the Hallimond tube and the flotation started with nitrogen flowrate at 100 ml per minute.

After the quartz was floated for 30 seconds, the flotation concentrate and tail were transferred to dry beakers (weigh them first) and dried in an oven at 110°C for 36 hour.

The weights of dry products can be obtained by subtracting the weight of empty beak from the total weight of beaker with the product.

4 Results and discussion

4.1 Determination of testing conditions

4.1.1 i.e.p. measurement of quartz





The zeta potential is a key parameter of solid particles in slurry during adsorption process. In aqueous suspensions, quartz particles become hydrated to form surface silanol groups whose dissociation generates surface charges on quartz particles. The sign and magnitude of the quartz surface charge have a significant effect on DAH adsorption. By manipulating the pH of solution, the sign and magnitude of the surface charge of quartz can be adjusted. The inset of Figure 4.1 shows the zeta potential of quartz particles (-38 micron size fraction) as a function of pH measured by the ZetaView. The iso-electric point (i.e.p.) of the quartz sample is at pH 2.0. The i.e.p. value also suggests that the surfaces of the quartz sample are free from major impurities.

4.1.2 i.e.p. of DAH precipitate

The Figure 4.1 above illustrates the zeta potential of DAH precipitate at different pH values at a DAH concentration of 2×10^{-4} M. The precipitate was produced using two procedures: one by increasing the pH of a true DAH solution until the pH of precipitation was exceeded; and the other one by adding DAH crystals to a background NaCl solution at a high pH. It should be noted that the results are restricted to high pH values, where amine forms a precipitate. As can be seen from the graph, the i.e.p. of the tested DAH precipitate is just below pH 11 regardless of how the solid amine was introduced for testing. However, the absolute zeta potential values are lower for the precipitated colloids compared to the crystals. Since it is very difficult to control the size of the amine particles during precipitation, it is possible that the difference in the absolute zeta potential values results from differences in the sizes of the tested amine colloids. At the same time, the obtained i.e.p. values agree very well with the electrokinetic data for DAH precipitates.

The experimental results of Laskowski et al. (1988) on the electrophoretic mobility versus pH for DAH suggest that the zeta potential curve and the i.e.p. of DAH precipitate move slightly towards more alkaline pH values near pH 11 with an increase in the concentration of the original DAH solution from which the precipitates were formed.

4.1.3 Settling time

After adsorption tests, the quartz settled quickly to the bottom of a Nalgene bottle and formed the sediment. It was clearly seen that the slurry was separated into two layers: a clear solution at the top and the sediment at the bottom, as shown earlier in Figure 3.4. To determine the settling time of the sample suspension before taking upper clear solution for TOC analysis, a turbidity-versus-time chart was built at solution pH 6 and 11. The purpose of the test was to assess how much time was needed for the quartz particles to settle out of suspension. Since the density of amine precipitates is lower than the density of water, all amine was expected to remain in suspension for subsequent TOC analysis. As shown in Figure 4.2, when

the slurry settled for 1 minute, the turbidities of both slurries at pH 6 and pH 11 were very low and couldn't decrease significantly by extending settling time. Thus, the settling time of slurry for all adsorption tests was set at 1 minute.





It is to note, however, that during the period of slurry settling, the adsorption of DAH onto quartz was still expected to continue.

4.1.4 Adsorption using Bottle roll and shaker

The purpose of comparing adsorption results using bottle roll method and shaker method is to assess the influence of hydrodynamic conditions on amine adsorption, particularly in the presence of amine precipitates. The shaker method offers more intense mixing conditions than the bottle roller set up. In the bottle roller test, the Nalgene bottle rotates at a very low speed to create relatively static conditions. The diagram shown in Figure 4.3 was plotted for DAH adsorption on quartz at varying pH using the bottle roller method and the shaker method. It was shown that adsorption amount dramatically increased above pH 8 until pH 11, then decreased above pH 11 for both tests. The two curves almost overlap in the tested pH range. The results indicate that the different hydrodynamic conditions of the experimental methods did not have a significant effect on the adsorption results.



Figure 4.3 Adsorption tests using bottle roll method and shaker method

There is a concern that aggregated DAH precipitates at higher pH might mechanically be buried in the quartz sediment when sampling the supernatant for TOC measurement. The adsorption densities of dodecylamine shown in Figure 4.3 are nearly same for both tests, even when DAH precipitate exists above the pH of precipitation (pH_{precip} =9.68). This observation indicates that dodecylamine aggregates did not get entrained in the quartz sediment to any significant degree at the bottom of Nalgene bottle during the adsorption tests.

4.1.5 Adsorption isotherm of DAH on quartz



Figure 4.4 Adsorption isotherm of DAH on quartz at pH 6 and pH 11

Figure 4.4 shows the adsorption density of DAH as a function of the initial DAH concentration at pH 6 and pH 11 respectively. At pH 6, when DAH concentration is below 2×10^{-4} M, the curve shows a slow increase in adsorption resulting from electrostatic interaction between the cationic DAH molecules and the negatively charged quartz surface. When the DAH concentration exceeds 2×10^{-4} M, the slope of adsorption density curve becomes steeper, because both electrostatic interaction between positively charged DAH ions and negatively charged quartz surface and lateral interactions between the densely adsorbed hydrocarbon chains of DAH contribute to the adsorption process (Somasundaran and Krishnakumar, 1997). At pH 11, the adsorption density curve increases quickly up to 2.5×10^{-3} M, then slope of the curve tends to level off. Based on these results, two DAH

concentrations were selected for further detailed research: 2×10^{-4} M and 1.75×10^{-3} M. A DAH concentration of 2×10^{-4} M was selected because of the sharp increase in adsorption occurring near that amount, and the adsorption density was well below a plateau/saturation value. In contrast, at 1.75×10^{-3} M of amine, the adsorption density of DAH was just below the apparent maximum adsorption density and the quartz surface was expected to be nearly fully covered by the amine.



4.1.6 Bubbling test



One of the prerequisites for an increase in adsorption of DAH on quartz particles as a result of collisions between gas bubbles and quartz particles is that DAH should be adsorbed onto gas bubbles before DAH transfer can take place between the bubbles and the quartz surface. The ability of gas bubbles to adsorb and carry amine was tested by bubbling nitrogen through an amine solution placed in a Hallimond tube. It is clearly shown in Figure 4.5 that the adsorption amount of DAH on nitrogen bubbles increases with bubbling time at both pH 6 and pH 11. At pH 11, the adsorption amount of DAH on bubbles is much larger than that at pH 6 particularly at shorter bubbling times. The main reason behind this difference is that at pH 11 amine is precipitated in the form of colloidal particles which are much larger (and carry more mass) than dissolved surfactant molecules at pH 6. As a result, adsorption of a single colloidal particle at pH 11 gives a much higher adsorption density than the adsorption of a single amine molecule.

The experimental errors of DAH precipitate adsorption on bubbles at pH 11 from triplicate tests are larger than the errors at pH 6, and the difference can primarily be attributed to difficulties with reproducing the same sizes of the colloidal precipitates for the adsorption tests.

4.2 Adsorption tests with and without nitrogen gas introduced

The Shimadzu TOC analyzer has a detection limit of 5 ppb of TOC, so very small changes and differences in DAH surfactant concentration can be detected. This feature was found to be particularly useful for measuring the residual DAH concentrations for comparative tests performed with and without gas bubbles in the system to determine their contribution to the amine adsorption process. The research results revealed that the amount of DAH adsorption by gas bubbles varied greatly depending on solution chemistry.

The experimental results are presented in the following tables as a mass balance of amine during four types of amine depletion experiments:

Test 1: <u>Adsorption measured by mixing in a shaker (30 minutes)</u>. This was a typical adsorption test performed in a table shaker described in section 3.2.4. Quartz was mixed with an amine solution in a Nalgene bottle and the mixture was conditioned for 30 minutes in a lab shaker.

Test 2: <u>Apparent adsorption on gas bubbles during bubbling in Hallimond tube (no quartz) (30 seconds).</u> This was a bubbling test in which nitrogen bubbles were passed through the tested amine solution in a Hallimond tube in the absence of any quartz. The objective of the test was to assess the amount of amine removed from

solution by the gas bubbles under the experimental conditions.

Test 3: <u>Adsorption on quartz measured by mixing in Hallimond tube (2 minutes)</u>. This was an adsorption test on quartz performed in a Hallimond tube using the same solution volume and mixing settings as in the bubbling test (Test 2). The main difference between this test and Test 1 was in the timescale of the test. Test 1 took 30 minutes while Test 3 was very short, about 2 minutes. The timescale was the same as the conditioning time during an actual flotation test.

Test 4: <u>Apparent adsorption measured during flotation in Hallimond tube (2 minutes</u> <u>conditioning followed by 30 sec of bubbling)</u>. In this experiment, a regular flotation test was carried out after which the amount of amine left in solution (tailings slurry) was measured. The result of this test reflects the total amount of amine removed from solution: by adsorption on quartz particles plus by adsorption on gas bubbles.

From the above descriptions, it should be apparent that the sum of amine removed from solution by adsorption on quartz (Test 3) and the amount of amine removed from solution by gas bubbles (Test 2) should be equal to the result of Test 4, if there is no extra transfer of amine to the flotation concentrate. Further analysis of the data is based on this type of comparison between the expected/calculated amount from Tests 2 and 3, and the actual measurement from Test 4.

The data in Table 4.1 showed that at a low DAH concentration of 2×10^{-4} M at pH 6, the adsorption density on quartz surface can potentially be increased by bubble-particle collision, provided that the bubbles carry amine molecules that can be transferred to the quartz surface, when the adsorption density on the quartz surface at a DAH concentration of 1.75×10^{-3} M is higher than that at the point of zeta potential reversal (PZR).

As shown in Table 4.3 and 4.4, at pH 11, at DAH concentrations of 2×10^{-4} M and 1.75×10^{-3} M, when nitrogen gas was introduced into the slurry after mixing in Hallimond tube for 2 minutes, the adsorption density of quartz actually decreased by bubble-quartz collision. The decrease in adsorption amount at concentration of 1.75×10^{-3} M is more significant than that of 2×10^{-4} M. The bubbles have negative effect on the increase in DAH precipitate adsorption on quartz.

4.2.1 Adsorption tests at pH 6

As can been seen in Table 4.1, the DAH fraction of TOC removed from solution after test increased from 6.1% to 10.9% after gas bubbles were introduced into the solid-liquid adsorption system. The adsorption density of DAH on quartz particles increased 65% when comparing result of adsorption measured during flotation and adsorption measured by mixing in Hallimond tube. The adsorption amount increase after gas bubbles introduced into the flotation system clearly indicate significant effect of gas bubbles in quartz flotation at DAH concentration of 2.0×10^{-4} M at pH 6.

This result in Table 4.1 supports the hypothesis of Digre and Sandvik (1968) that under normal flotation conditions the adsorption density of surface-active collectors on mineral particles is enhanced by transfer of collector from the gasliquid interface to the solid-liquid interface. The adsorption densities measured in the solid-liquid system are not representative of the solid-liquid-gas system.

The results in Table 4.2 show that the introduced gas bubbles in the flotation system had a negligible effect on DAH adsorption on the quartz surface at a DAH concentration of 1.75×10^{-3} M at pH 6. The total amount of DAH removed from solution after floating quartz for 30 seconds was equal to the sum of the amount of DAH adsorbed onto air bubbles (as determined from the bubbling test) and the amount of DAH adsorbed on quartz particles in the adsorption test carried out in the Hallimond tube.

To interpret the effect of air bubbles on DAH adsorption on quartz in the three-phase gas-solid-liquid system, it is important to understand the chemistry of DAH solution, the adsorption characteristics of quartz and air bubbles, electrostatic characteristics of quartz particles and air bubbles, and interactions (collisions, attachment, etc.) between quartz particles and gas bubbles.

Type of adsorption test (testing time)	Nominal TOC of initial DAH solution before test, mg/l	Average residual TOC of solution after test, mg/l	Standard deviation of triplicate tests, mg/l	Fraction of TOC removed from solution after test, %	Apparent adsorption density of DAH, mol/cm ²
Test 1. Adsorption measured by mixing in shaker (30 min)	28.8	25.6	0.02	11.0	1.5X10 ⁻¹⁰
Test 2 . Apparent adsorption on gas bubbles during bubbling in Hallimond tube (no quartz) (30 sec)	28.8	28.6	0.02	0.6	N/A
Test 3 . Adsorption on quartz measured by mixing in Hallimond tube (2 min)	28.8	27.0	0.07	6.1	8.5X10 ⁻¹¹
Test 4. Apparent adsorption measured during flotation in Hallimond tube (2 min conditioning followed by 30 sec of bubbling)	28.8	25.7	0.81	10.9	1.4X10 ⁻¹⁰

Table 4.1 Initial DAH concentration of 2×10^{-4} M at pH 6 adsorption test result, fine quartz (BET specific surface area 0.15 m²/g)

Type of adsorption test (testing time)	Nominal TOC of initial DAH solution before test, mg/l	Average residual TOC of solution after test, mg/l	Standard deviation of triplicate tests, mg/l	Fraction of TOC removed from solution after test, %	Apparent adsorption density of DAH, mol/cm ²
Test 1. Adsorption measured by mixing in shaker (30 min)	252.2	244.1	0.33	3.2	3.7X10 ⁻¹⁰
Test 2 . Apparent adsorption on gas bubbles during bubbling in Hallimond tube (no quartz) (30 sec)	252.2	249.1	0.67	1.2	N/A
Test 3 . Adsorption on quartz measured by mixing in Hallimond tube (2 min)	252.2	248.0	0.57	1.7	1.9X10 ⁻¹⁰
Test 4. Apparent adsorption measured during flotation in Hallimond tube (2 min conditioning followed by 30 sec of bubbling)	252.2	245.0	0.63	2.9	1.9X10 ⁻¹⁰

Table 4.2 Initial DAH concentration of 1.75×10^{-3} M at pH 6 adsorption test result, fine quartz (BET specific surface area 0.15 m²/g)



Figure 4.6 Species distribution diagram of dodecylamine in aqueous at total concentration of 2×10^{-4} M and 1.75×10^{-3}



Figure 4.7 Correlation of adsorption, contact angle, flotation response and zeta potential for quartz as a function of dodecylammonium acetate concentration at pH 6 to 7, 20 to 25 °C (Fuerstanau, 1997, as cited in Somasundaran, 2006))

According to equation 2-2 to equation 2-5, the species distribution diagram of DAH at total dodecylamine concentrations of 2×10^{-4} M and 1.75×10^{-3} M was constructed in Figure 4.6. The Figure shows the DAH precipitate pH is 9.68 at concentration of 2×10^{-4} M and 8.69 at concentration of 1.75×10^{-3} M. The pKa for both of DAH solutions is 10.63.

At low concentration of DAH and neutral pH 6 to 7, when dodecylammonium cations dominate in DAH solutions (see Figure 4.6), the dodecylammonium cations were individually physically adsorbed onto the negatively charged quartz surface through electrostatic interaction without lateral chain-chain association. The zeta potential of quartz remains negative and rather unaffected by the low amine concentrations. When the DAH concentration increases above 10⁻⁴ M (Somasundaran & Zhang, 2006), a sharp increase in the adsorption density occurs resulting from the onset of formation of hemimicells at the solid-liquid interface through association of the hydrocarbon chains (tails) of the adsorbed dodecylammonium cations until the DAH concentration is near the bulk CMC value of about 1.46 \times 10⁻² M (Mukerjee & Mysels, 1971). This marked increase in the adsorption density on the quartz surface is accompanied by a sharp increase in the contact angle, flotation recovery, and zeta-potential (Figure 4.7). In this DAH concentration range, lateral inter-chain association is the main driving force for the increasing adsorption of DAH on quartz. When the bulk DAH concentration is at or near CMC, micelles start forming in solution, and bilayer adsorption starts taking place at the quartz surface through inter-chain association. In this case, however, the second layer of the adsorbed amine molecules is oriented with their functional away from the quartz surface. The driving force for this type of bi-layer adsorption is the same as that for the formation of micelles in bulk solution (Fuersteanu and Jia 2004).



Figure 4.8 Schematic representation of the physisorption of an aqueous cationic surfactant on a negatively charged solid (Fuerstenau & Jia 2004)

The point of zeta potential reversal from negative to positive (PZR) for guartz at neutral pH is at a DAH concentration of 7×10^{-4} M (Albijanic et al., 2014), at which the charge adsorbed in the Stern layer equals to the surface charge of quartz, indicating that the hydrophobicity of quartz particles reaches a maximum level. In the concentration range from 1 \times 10⁻⁴ M (Fuersteanu and Jia, 2004) to 2 \times 10⁻⁴ M (Albijanic et al., 2014) which is below the PZR, formation of hemimicells begins (in region II), the driving force for adsorption is enhanced by the onset of lateral hydrocarbon interactions between the adsorbed surfactant molecules in addition to attractive electrostatic interactions between dodecylammonium cations and the negatively charged quartz surface. The slope of the adsorption curve reaches a maximum value. There are adequate negatively charged adsorption spots on quartz surface for deposition of DAH cations. The net surface charge of quartz particles below PZR is negative. At a DAH concentration of 1.75×10^{-3} M, which is above PZR (in region III), the quartz surface was very likely electrically neutralized by adsorbed dodecylammonium cations, and bi-layer adsorption started to contribute to the adsorption process by chain-chain interaction between the anchoring adsorbed layer of amine molecules and additional amine molecules from bulk solution. This reverse orientation of amine molecules made the quartz particles positively charged.

It has been known that gas bubbles are charged in aqueous solution and charges on gas bubbles can be influenced by dissolved electrolyte/surfactant species and solution pH. In distilled water, the electrical charge of the gas-water interface is attributed to a greater excess of H⁺ and OH⁻ ions at the interface than in

the bulk solution. Microbubbles are negatively charged under a wide range of pH values indicating the OH- ions are more effectively adsorbed at the interface than H+. with an i.e.p. value at pH 4.5 (Takahashi, 2005). Huddleston and Smith (1976, as cited in Healy et al., 2007) reported an i.e.p. value at pH 2 at nitrogen-aqueous interface, which was due to exceedingly strong specific adsorption of OH⁻ or due to a larger shift of the interfacial water ionization constant by more than six decades from that in bulk water. In NaCl solution as a strong electrolyte at neutral pH, Na⁺ and Cl ions do not specifically adsorb at the gas-liquid interface and an i.e.p. of air bubble at pH 1.5 can be obtained by extrapolating the curves at different NaCl concentrations in the pH range studied (Li and Somasundaran, 1991). The decrease in the magnitude of the zeta potential of gas bubbles at higher ionic strengths, when for example NaCl is added to distilled water, is caused by Na+ counter-ions entering into the double layer to neutralize the negatively charged gas bubbles. For weak electrolyte solutions, such as those of dodecylamine, the charges of bubbles were found to be, depending pH, either positively or negatively charged (Laskowski, Yorda and Yoon, 1989).

The pH values of precipitation of DAH at the tested concentrations of 2×10^{-4} M and 1.75×10^{-3} M are 9.7 and 8.7, respectively. At pH 6, dodecylammonium cations are the predominant species in solution for both DAH concentrations of 2×10^{-4} M and 1.75×10^{-3} M. When gas bubbles are introduced into a DAH solution, bubbles are covered with dodecylammonium cations, which change the zeta potential of gas bubbles from negative to positive. A further increase in DAH concentration in solution also increases the adsorption density of amine on the bubble surfaces. As a result, the zeta potential of bubbles at a DAH concentration of 1.75×10^{-3} M is more positive than at a concentration of 2×10^{-4} M. This trend also can be seen in the literature data shown in Figure 2.10 (Laskowski et al., 1989).

According to the above analysis, the DAH transfer process from bubbles to quartz during hemimicells formation period (region II and region III) can be described as follows.

At a DAH concentration of 2 \times 10⁻⁴ M, when the quartz surface is only partially covered by the surfactant, and there are still negatively charged vacant sites

available for adsorption by collision between bubbles and quartz. At the same time, gas bubbles can be expected to be positively charged as a result of amine adsorption (Figure 4.10). As a result, the electrostatic double layers of bubble and quartz with oppositely charged zeta potentials overlap. When bubbles and particles collide a three-phase aggregate/system is created, with a combined interaction of electrostatic attractive force between bubble and guartz, and lateral attractive forces between hydrocarbon chains of DAH molecules and cations. The DAH cation adsorbed on the bubble surface, with its positively charged ammonium group directed towards the solution, can be transferred onto the negatively charged vacant sites on the quartz surface. The quartz particles that drop back from the froth phase due to bubble coalescence, bubble bursting, etc. may repeatedly collide with more bubbles and acquire additional collector from the bubble surfaces upon collisions. It should be noted that such repeated collisions do not occur under the conditions of Test 3 (adsorption on quartz) and obviously no collisions can take place during the bubbling test (Test 2). As a result, these multiple collisions between bubbles and particles that take place only under actual flotation conditions are the main source of the difference between the expected amount of amine removed from solution during flotation (calculated from the results of Tests 2 and 3) and the actual amount measured during a flotation test (Test 4). The increase in adsorption density of quartz increase hydrophobicity of quartz, thus improves quartz recovery. The flotation recovery at DAH concentration of 1.75×10^{-3} M is 95.2%, which is higher than the recovery of 88.8% at concentration of 2×10^{-4} M.

At a DAH concentration of 1.75×10^{-3} M, the zeta potential of quartz can be expected to be positive, which also indicates that amine adsorption with formation of hemimicells in region 2 was completed and that additional adsorption of amine molecules could proceed only through tail-to-tail interactions resulting in the formation of a second layer of amine molecules adsorbed now with the head group pointing away from the quartz surface. Under these conditions, there are very few free adsorption sites on the quartz surface available for further amine adsorption. In addition, the positive zeta potential of the quartz particles should also inhibit further adsorption of the cationic surfactant.

At the same time, gas bubbles can also be expected to be positively charged at such a relatively high amine concentration. Amines adsorb on gas bubbles with their polar charged head groups oriented towards the solution phase, thus imparting a positive zeta potential to the bubble. When the quartz particles collide with bubbles, the repulsive electrostatic interaction between the now positively charged double layers of quartz and bubbles, in addition to the lack of free adsorption sites the quartz surface, prevents DAH adsorption on quartz by transfer from the bubble surfaces. Furthermore, DAH cations adsorbed on bubbles orient their polar parts towards solution are also detrimental to the further transfer of DAH cations to quartz.

Repeated collisions between quartz particles and bubbles favor DAH transfer from the bubble surface to the quartz surface. The data reported by Roe-Hoan and Laiqun (1996) show that the hydrophobic attractive force plays the most important role in decreasing the energy barrier for bubble-particle attachment. Thus, the probability of bubble-particle adhesion at a DAH concentration of 2×10^{-4} M, when the hydrophobic force is smaller due to the lower adsorption density of DAH cations, is much smaller than that at a DAH concentration of 1.75×10^{-3} M. In turn, the lower probability of bubble-quartz adhesion increases the number of collisions between quartz particles and air bubbles, which seems to facilitate the transfer of DAH from bubbles to quartz during quartz flotation at the lower DAH concentration.

The experimental results presented in this thesis agree with the experimental data of successive flotation experiments on Pyrex glass particles in the Hallimond tube, described by Fuerstenau (2001). The flotation of Pyrex glass particles was carried out at dodecylammonium acetate (DAA) concentrations of 5×10^{-5} M, 1×10^{-4} M and 5×10^{-4} M at pH 6.5. At each DAA concentration, after each flotation experiment, the pulp was agitated inside the Hallimond tube until all bubbles were detached from the particles, and then the procedure was repeated for 21 successive flotation runs. The flotation data showed an increase in the flotation rate with increasing number of consecutive flotation tests until a constant flotation rate was eventually reached for each DAA concentration. The increase in the flotation rate was attributed to excess adsorption of DAA molecules that were transferred to the solid-air interface from the bubble surface upon contact (Fuerstenau, 2001).

4.2.2 Adsorption at pH 11

For DAH concentrations of 2×10^{-4} M and 1.75×10^{-3} M at pH 11, the solubility limit is exceeded, and the DAH true solution at pH 6 transitions to a colloidal system at pH 11. As shown in a species distribution diagram for dodecylamine (Figure 4.6), the concentrations of dodecylammonium cations (RNH₃⁺) and cation-molecule complexes (RNH₃⁺·RNH₂) decrease sharply above the pH value of precipitation, while the concentration of free dodecylamine precipitate molecule increases and asymptotically reaches a plateau concentration of C_T - S (total amine added minus solubility limit). The DAH precipitate species can accumulate at the quartz-liquid and bubble-liquid interfaces and make the properties of the flotation system differ from that in true solution at pH 6.





Figure 4.9 Colloidal precipitate aggregates at a DAH concentration of 2×10^{-4} M (left) and 1.75×10^{-3} M (right) at pH 11. Due to the lower density of solid amine compared to the density of water, gradual accumulation of the precipitate at the solution surface is clearly visible.

Type of adsorption test (testing time)	Nominal TOC of initial DAH solution before test, mg/l	Average residual TOC of solution after test, mg/l	Standard deviation of triplicate tests, mg/l	Fraction of TOC removed from solution after test, %	Apparent adsorption density of DAH, mol/cm ²
Test 1. Adsorption measured by mixing in shaker (30 min)	28.8	4.9	0.07	82.9	1.6X10 ⁻⁹
Test 2 . Apparent adsorption on gas bubbles during bubbling in Hallimond tube (no quartz) (30 sec)	28.8	23.3	0.13	19.2	N/A
Test 3 . Adsorption on quartz measured by mixing in Hallimond tube (2 min)	28.8	5.6	0.27	80.6	1.1X10 ⁻⁹
Test 4. Apparent adsorption measured during flotation in Hallimond tube (2 min conditioning followed by 30 sec of bubbling)	28.8	5.1	0.09	82.1	8.9X10 ⁻¹⁰

Table 4.3 Initial DAH concentration of 2×10^{-4} M at pH 11 adsorption test result, fine quartz (BET specific surface area 0.15 m²/g)

Type of adsorption test (testing time)	Nominal TOC of initial DAH solution before test, mg/l	Average residual TOC of solution after test, mg/l	Standard deviation of triplicate tests, mg/l	Fraction of TOC removed from solution after test, %	Apparent adsorption density of DAH, mol/cm ²
Test 1. Adsorption measured by mixing in shaker (30 min)	252.2	14.7	0.54	94.2	1.2X10 ⁻⁸
Test 2 . Apparent adsorption on gas bubbles during bubbling in Hallimond tube (no quartz) (30 sec)	252.2	206.4	0.91	18.2	N/A
Test 3 . Adsorption on quartz measured by mixing in Hallimond tube (2 min)	252.2	109.7	17.88	56.5	7.0X10 ⁻⁹
Test 4. Apparent adsorption measured during flotation in Hallimond tube (2 min conditioning followed by 30 sec of bubbling)	252.2	135.5	0.73	46.3	3.7X10 ⁻⁹

Table 4.4 Initial DAH concentration of 1.75×10^{-3} M at pH 11 adsorption test result, fine quartz (BET specific surface area 0.15 m²/g)

The adsorption results obtained through Test 1 (mixing for 30 min without gas) at DAH concentrations of 2 \times 10⁻⁴ M and 1.75 \times 10⁻³ M in Table 4.3 and Table 4.4 show very high adsorption densities of DAH on quartz. When expressed as a percentage of the total DAH added, the amount adsorbed increases from 11.0% at pH 6 to 82.9% at pH 11 for a DAH concentration of 2×10^{-4} M, and from 3.2% at pH 6 to 94.2% at pH 11 for a DAH concentration of 1.75×10^{-3} M. As shown in Figure 4.1, the i.e.p. for DAH precipitate is situated near pH 11. Due to the net-zero surface charge on the colloidal particles of the precipitate, the precipitate particles are more likely to coagulate into larger precipitate aggregates when solution pH is at i.e.p. of DAH than when they are charged at pH values away from the i.e.p. When the quartz particles are introduced into the DAH colloidal precipitate system at pH 11, DAH adsorption on quartz is primarily due to coagulation between large DAH precipitate aggregates and the fine quartz particles. Thus, the adsorption density under conditions of precipitation (pH 11) is much higher than the adsorption density from true solutions. The adsorption of a single large colloidal particle on quartz will result in a much higher mass adsorbed compared to the adsorption of a single surfactant molecule of a much lower mass.

It is interesting to note that the adsorption density of the precipitate, when expressed as a percentage of the total amount of amine, without air at a DAH concentration of 1.75×10^{-3} M at pH 11 is 10 times higher than that at a concentration of 2×10^{-4} M, which is almost equal to the ratio of the initial concentrations used in the tests ($1.75 \times 10^{-3}/2.0 \times 10^{-4}$). The relationship between the adsorption density and the DAH concentration is almost linear. This observation indicates that the adsorption capacity of quartz under precipitation conditions is determined by net-uncharged DAH precipitates adsorbed on the quartz surface. Since electrostatic attraction between the neutral precipitate aggregates and the negatively-charged quartz particles can be expected to be very weak, the adsorption process is dominated by hydrogen bonding between colloidal particles of the precipitate and the silanol groups (-OH) on the quartz surface.

The adsorption densities of DAH on the quartz particles shown in Table 4.3 and Table 4.4 decrease for both DAH concentrations of 2×10^{-4} M and 1.75×10^{-3} M

at pH 11 when nitrogen gas was introduced into the DAH-quartz system. At pH 11, when neutral DAH precipitates dominate in solution, both the quartz particles and bubbles are covered by the partially hydrophobic DAH precipitates. As a result, they acquire almost identical electrokinetic potentials, as can be seen from the data shown in Figure 4.10 (Laskowski et al., 1989). Kou, Tao and Xu, (2010), using a high sensitivity surface characterization technique referred to as the quartz crystal microbalance with dissipation technique revealed that the DAH precipitate on quartz was a thick and soft dissipated multilayer structure at pH values above the pH of precipitation. Because of lack of electrostatic attraction between quartz particles and bubbles, in addition to weak hydrophobicity of DAH precipitate in this case, the flotation response is worse than that at pH 6. The flotation recovers at pH 11 is 55.1% and 74.2% for DAH concentration of 1.75×10^{-3} M and 2×10^{-4} M respectively.



Figure 4.10 Effect of pH on electrophoretic mobility of microbubbles and quartz particles in the presence of dodecylamine hydrochloride (Laskowski, 1989)

It should be observed from Table 4.3 and Table 4.4 that the amount of amine removed from solution under flotation conditions at pH 11 (Test 4) is actually lower than the combined amounts removed during the adsorption test on quartz (Test 3) and by bubbling nitrogen through the amine solution (Test 2). When bubbles are introduced into the quartz-DAH system, it is possible that a portion of DAH precipitates carried by the bubbles and quartz particles to the froth zone detach and fall back into the slurry phase as quartz-laden bubbles burst and coalesce in the froth zone. In this scenario, both quartz particles and colloidal precipitate aggregates fall back into the slurry phase. Re-attachment by repeated collisions may not be efficient in this case since strong electrostatic attraction does not operate between the quartz particles and precipitate aggregates. The dynamic conditions of flotation mechanically remove colloidal aggregates from the froth concentrate.

5 Conclusions and future work

A series of adsorption tests with and without nitrogen gas introduced were carried out at different concentration of DAH and pH's using the solution depletion method in Hallimond tube flotation to investigate the role of gas bubbles on DAH transfer during bubbles-particles collision. The following major conclusions were derived from this study:

1. At pH 6, at a low concentration of 2×10^{-4} M near the onset of hemimicelle formation at the quartz-liquid interface, DAH can be transferred to the quartz surface by repeated particle-bubble collisions. A partial DAH coverage of the quartz surface, hydrocarbon chain-chain lateral interactions, and electrostatic attraction between the negatively charged quartz surface and the positively charged gas bubbles combine for a driving force for the transfer process. In contrast, at a high concentration of 1.75×10^{-3} M when the coverage of the quartz surface is nearly complete, the transfer of amine between gas bubbles and the quartz surface is much less favorable. In this case, the onset of bi-layer adsorption of amine and electrostatic repulsion between the positively charged gas bubbles and the positively charged quartz surface further inhibit the transfer process.

2. At pH 11, when amine extensively precipitates from solution, both bubble surfaces and quartz particles are coated with neutral DAH colloidal precipitates at both amine concentrations. Under the dynamic flotation conditions, when nitrogen gas was introduced into such a DAH colloidal precipitate system, the DAH precipitate was initially carried to the froth zone by both gas bubbles and quartz particles. However, bubble rupture and coalescence in the forth zone led to partial detachment of the colloidal precipitate, and the colloidal precipitate particles fell back to the solution phase. In contract to true solution conditions at pH 6, re-attachment and re-entry onto the froth zone were partly prevented by the lack of electrostatic attraction between the nearly uncharged colloidal precipitate and the negatively charged quartz surface. The precipitate appears to have a stronger affinity towards the bubbles than towards the quartz surface.

3. Overall, transfer of amine between bubbles and quartz particles is possible only under true solution conditions, or in the absence of colloidal precipitates, and when the quartz surface possesses sufficient space to accommodate additional surfactant molecules. Dense and multilayer adsorption of the surfactant occurring at higher amine dosages substantially prevents the transfer process. Electrostatic repulsion and/or attraction between the bubbles and the quartz surface play a significant role in the transfer process.

Because of detection limit of experimental instruments, more studies at DAH concentration below 2 \times 10⁻⁴ M, when the electrostatic attraction force dominate adsorption process, should be follow up in future research work.
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Appendices







Appendix 2 Calibration curves of DAH concentration versus TOC reading below 100 -400mg/l

Appendix 3 TC calibration curve at concentration below 100 mg/l

TOC-V Cal Curve Information C:\TOC3201\CalCurves\Yan-TC-100_10-Sep2014.2014_09_10_03_04_55.cal

Date of Creation	4:32:12 AM 9/10/2014
User	
System	TOC-V ASI-V

Cal. Curve

Sample Name: Sample ID: Object ID Cal. Curve: Status Comment:

TC 100-10ppm calibration curve Untitled 0A-100497-10101000-133536D36ABF-0000 Yan-TC-100_10-Sep2014.2014_09_10_03_04_55.cal Completed

Туре	Anal.
Standard	TC

Conc: 100.0mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	543.9	50uL	1	*******		9/10/2014 3:11:30 AM
2	542.0	50uL	. 1	******		9/10/2014 3:14:42 AN

0.000%

11

Acid Add.	0.000%
Mean Area	543.0
SD Area	1.344
CV Area	0.25%
Vial	11

Conc: 50.00mg/L

No.	Area	Inj. Vol.	Aut.	Rem.	Ex.	Date / Time
1	270.9	50ul	Dil. 2	******		9/10/2014 3:22:36 AM
2	263.1	50uL	2	******	E	9/10/2014 3:25:39 AM
3	270.9	50uL	2	******		9/10/2014 3:28:43 AM

Acid Add.	0.000%
Mean Area	270.9
SD Area	0.000
CV Area	0.00%
Vial	11

Conc: 33.33mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	177.3	50uL	3	******		9/10/2014 3:38:37 AM
2	174.4	50uL	3	******		9/10/2014 3:41:47 AM
Acid Mea SD / CV /	Add. n Area Area Area		0.000 175.9 2.051 1.179	%		
Vial			12			

Conc: 25.00mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	129.6	50uL	4	******		9/10/2014 3:49:34 AM
2	131.4	50uL	4	*******		9/10/2014 3:52:36 AM

Acid Add.	0.000%
Mean Area	130.5
SD Area	1.273
CV Area	0.98%
Vial	12

Conc: 20.00mg/L

No.	Area	Inj. Vol.	Aut.	Rem.	Ex.	Date / Time
		-	Dil.			
1	100.9	50uL	5	******		9/10/2014 4:02:21 AM
2	100.5	50uL	5	******		9/10/2014 4:05:23 AM

Acid Add.	0.000%
Mean Area	100.7
SD Area	0.2828
CV Area	0.28%
Vial	13

Conc: 16.67mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	86.24	50uL	6	******	E	9/10/2014 4:13:13 AM
2	81.89	50uL	6	******		9/10/2014 4:16:21 AN
3	81.23	50uL	6	******		9/10/2014 4:19:32 AN

rona ritatan	0.00070
Mean Area	81.56
SD Area	0.4667
CV Area	0.57%
Vial	13

Conc: 10.00mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	50.12	50uL	10	******		9/10/2014 4:28:55 AN
2	49.62	50uL	10	******		9/10/2014 4:32:12 AN

Acid Add.	0.000%
Mean Area	49.87
SD Area	0.3536
CV Area	0.71%
Vial	14

Slope:	5.491
Intercept	0.000
r^2	0.9999
r	1.0000
Zero Shift	Yes

Area	604.024	9	1	9	1		1	1	9	1	- 1	T	1	7		
	500			1-1-					1-1			7				
	400		1	1	1			1		1		1	1			
	300		1					1		+		1		_		
	200			1-1		2			1-1							
	100		-	7			1	1		1	1	1	1	_		
	0	22	T -1-	1-1				1-1-	1-1	-1-			1-1			
		0.	10	20	30	40	50	60	70) 8	0 9	90	100	110	Cor	ic[mg/L]

Appendix 4 TC calibration curve at concentration 100-400 mg/l

TOC-V Cal Curve Information C:\TOC3201\CalCurves\Yan-TC-400_100-Sep2014.2014_09_10_02_17_58.cal

Date of Creation	3:04:55 AM 9/10/2014
User	
System	TOC-V ASI-V

Cal. Curve

Sample Name: Sample ID: Object ID Cal. Curve: Status Comment:

TC 400-100ppm calibration curve Untitled 0A-100497-10101000-133536D36A9F-0000 Yan-TC-400_100-Sep2014.2014_09_10_02_17_58.cal Completed

Туре	Anal.
Standard	TC

Conc: 400.0mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	2232	50uL	1	*******		9/10/2014 2:25:04 AM
2	2218	50uL	1	*******		9/10/2014 2:29:01 AN

0.000%

9

Acid Add.	0.000%
Mean Area	2225
SD Area	9.899
CV Area	0.44%
Vial	9

Conc: 200.0mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	1112	50uL	2	******		9/10/2014 2:37:05 AM
2	1104	50uL	. 2	******		9/10/2014 2:40:41 AN

Acid Add.	0.000%
Mean Area	1108
SD Area	5.657
CV Area	0.51%
Vial	9

Conc: 133.3mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	728.1	50uL	3	******		9/10/2014 2:50:31 AN
2	727.0	50uL	3	******		9/10/2014 2:53:52 AM
Acid Mea	n Area		727.5	1% I		
SD /	Area		0.777	8		

72



2/2

Appendix 5 IC calibration curve at concentration below 10 mg/l

TOC-V Cal Curve Information C:\TOC3201\CalCurves\Yan-TC-100_10-Sep2014.2014_09_10_03_04_55.cal

Date of Creation	4:32:12 AM 9/10/2014
User	
System	TOC-V ASI-V

Cal. Curve

Sample Name: Sample ID: Object ID Cal. Curve: Status Comment: TC 100-10ppm calibration curve Untitled 0A-100497-10101000-133536D36ABF-0000 Yan-TC-100_10-Sep2014.2014_09_10_03_04_55.cal Completed



Conc: 100.0mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	543.9	50uL	1	******		9/10/2014 3:11:30 AM
2	542.0	50uL	1	******		9/10/2014 3:14:42 AM

Acid Add.	0.000%
Mean Area	543.0
SD Area	1.344
CV Area	0.25%
Vial	11

Conc: 50.00mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	270.9	50uL	2	******		9/10/2014 3:22:36 AM
2	263.1	50uL	2	******	E	9/10/2014 3:25:39 AM
3	270.9	50uL	2	*******		9/10/2014 3:28:43 AN

Acid Add.	0.000%
Mean Area	270.9
SD Area	0.000
CV Area	0.00%
Vial	11

Conc: 33.33mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	177.3	50uL	3	******		9/10/2014 3:38:37 AM
2	174.4	50uL	3	******		9/10/2014 3:41:47 AM

Mean Area	175.9
SD Area	2.051
CV Area	1.17%
Vial	12

Conc: 25.00mg/L

1/2

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	129.6	50uL	4	******		9/10/2014 3:49:34 AN
2	131.4	50uL	4	*******		9/10/2014 3:52:36 AN
Acid Mea SD / CV /	Add. n Area \rea \rea		0.000 130.5 1.273 0.989	1% 1 6		
Vial			12			

SD Area	1
CV Area	0
Vial	1

Conc: 20.00mg/L

No.	Area	Inj. Vol.	Aut.	Rem.	Ex.	Date / Time
			Dil.			
1	100.9	50uL	5	******		9/10/2014 4:02:21 AN
2	100.5	50uL	5	******		9/10/2014 4:05:23 AN

Acid Add.	0.000%
Mean Area	100.7
SD Area	0.2828
CV Area	0.28%
Vial	13

Conc: 16.67mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	86.24	50uL	6	******	E	9/10/2014 4:13:13 AM
2	81.89	50uL	6	******		9/10/2014 4:16:21 AM
3	81.23	50uL	6	******		9/10/2014 4:19:32 AM

Acid Add.	0.000%
Mean Area	81.56
SD Area	0.4667
CV Area	0.57%
Vial	13

Conc: 10.00mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	50.12	50uL	10	******		9/10/2014 4:28:55 AM
2	49.62	50uL	10	******		9/10/2014 4:32:12 AM

Acid Add.	0.000%
Mean Area	49.87
SD Area	0.3536
CV Area	0.71%
Vial	14

Slope:	5.491
Intercept	0.000
r^2	0.9999
r	1.0000
Zero Shift	Yes

Area	604.024	9	T	3	T	9	T	9	1	3	1.2		
	500										2		
	400		1	1-1-1	1	1	1		-				
	300						~		1				
	200				-								
	100		-	-	1		1		1	1	1		
	0		1	1- 1- 1									
	1	0 1	0 2	20 3	0 4	0 5	0 6	0 7	0 8	0 9	0 10	00 110	Conc[mg/L]

2/2

Appendix 6: Particle size distribution of quartz







Result Analysis Report

Sample Name: Lane Mt Quartz fo	mple Name: SOP Name: ne Mt Quartz for adsorption test Quartz-Frank							Measured: Tuesday, October 01, 2013 11:08:03 AM							
Sample Source & type: Measured by: Quartz = Lane Mt US contract Sample bulk lot ref: Result Source: 123-ABC Averaged							Analysed: Tuesday, October 01, 2013 11:08:05 AM								
Particle Name: Quartz, Avg Particle RI: 1.545 Dispersant Name: Water				Accesso Hydro 20 Absorpti 1 Dispersa 1.330	ry Name: DOS (A) on: nt RI:		Analysi General Size ran 0.020 Weighte 0.807	Analysis model: General purpose Size range: 0.020 to 2000.000 um Weighted Residual: 0.807 %				Sensitivity: Enhanced Obscuration: 14.98 % Result Emulation: Off			
Concentration: 0.1467 %Vo	bl			Span : 0.790				Uniform 0.246	nity:			Result units Volume	ult units: ume		
Specific Surface 0.0926 m²/g	Area:			Surface \ 64.800	Weighted um	Mean D[3,2]	:	Vol. We 70.716	ighted Mea um	n D[4,3]:					
d(0.1): 45.9	957	um	d(0.5): 67.	797	um	d(0.8):	87.706	um		d(0.9):	99.524	um		
5					Pi	article Size	Distribut	ion							
	20							^							
	18														
	16														
(%)	14 -														
e (12														
- En	10					_									
Vol	8	_													
	6														
	4														
	2														
	- -														
	0.0	1	0	.1	1		10	2	100	10	00 300	00			
						Particle S	Size (µm)								
-Lane	Mt Qu	artz for	r adsorp	tion test,	Tuesday	, October	01, 2013	11:08:03	AM						
Size (j	um) Volum 020	0.00	0.142	Volume In %	Size (µm) 1.002	Volume In %	5ize (µm) 7.096	/olume In %	50.238 Vo	lume in %	355.656	Volume In %			
0.	022	0.00	0.159	0.00	1.125	0.00	7.962	0.00	56.368	13.58	399.052	0.00			
0.	025	0.00	0.178	0.00	1.262	0.00	8.934	0.00	70.963	14.67	447.744 502.377	0.00			
0.	032	0.00	0.224	0.00	1.589	0.00	11.247	0.00	79.621	14.02	563.677	0.00			
0.	036	0.00	0.252	0.00	1.783	0.00	12.619	0.00	89.337	8.74	632.456	0.00			
0.	045	0.00	0.317	0.00	2.244	0.00	15.887	0.00	112.468	5.52	796.214	0.00			
0.	050	0.00	0.356	0.00	2.518	0.00	17.825	0.00	126.191	1.08	893.367	0.00			
0.	056	0.00	0.399	0.00	2.825	0.00	20.000	0.00	141.589 158.866	0.15	1002.374	0.00			
0.	071	0.00	0.502	0.00	3.557	0.00	25.179	0.00	178.250	0.00	1261.915	0.00			
	000	0.00	0.564	0.00	3.991	0.00	28.251	0.16	200.000	0.00	1415.892	0.00			
0.	080	0.00	0.000	0.00							1 1268 026				
0. 0. 0.	089	0.00	0.632	0.00	4.477	0.00	35.566	0.93	251.785	0.00	1782.502	0.00			
0. 0. 0.	080 089 100 112	0.00	0.632 0.710 0.796	0.00	4.477 5.024 5.637	0.00	35.566 39.905	0.93 2.47 4.91	224.404 251.785 282.508	0.00 0.00 0.00	1782.502 2000.000	0.00 0.00			
0) 0) 0. 0.	080 089 100 112 126 142	0.00 0.00 0.00 0.00	0.632 0.710 0.796 0.893 1.002	0.00 0.00 0.00 0.00	4.477 5.024 5.637 6.325 7.099	0.00 0.00 0.00 0.00	31.698 35.566 39.905 44.774 50.238	0.93 2.47 4.91 7.97	224.404 251.785 282.508 316.979 355.656	0.00 0.00 0.00 0.00	1782.502 2000.000	0.00			

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File name: Lane Mt Record Number: 52 10/1/2013 11:22:27 AM



Appendix 7: Quantachrome autosorb automated gas sorption report



Appendix 8: Zeta potential of quartz at pH 2.0

Appendix 9: Zeta potential of quartz at pH 3.0





Appendix 10: Zeta potential of quartz at pH 4.0



Appendix 11: Zeta potential of quartz at pH 6.7



Appendix 12: Zeta potential of quartz at pH 9.0

Appendix 13: Zeta potential of DAH (solid) precipitate at pH 10.89



Appendix 14: Zeta potential of DAH (solid) precipitate at pH 10.94

	Electrophoresis & Brownian Motion Video Analysis Laser Scattering Microscopy
	Operator (Report): zeta Video Operator: zeta
Sample Parameters Sample Name: DDA(Solid)-2X10-4M-pH 10.94 Comment: Put DDA.HCL solid into NaCl solution, Sample Checked: 2014-03-11 01:16:27 SL1 OK: OK, SL2 OK: OK, Number of Good Positions: 11 Electrolyte: NaCl, Concentration: 0.005 N Temperature: 23.94 °C sensed pH 10.9 entered Conductivity: 855.18 µS/cm sensed Measurement Parameters Coll S/N: 1141x15 7157	Result Mobility: 0.12 FWHM 0.60 μm/sec/V/cm, @ 25℃: 0.12 μm/sec/V/cm ZP Factor 13.1 (Smoluchowski): Zeta Potential @ 25 ℃: 1.56 FWHM 7.85 mV Quality Number of Traced Particles: 298 ΔSL: 5.93 mV
Sensed Electric Field: 3.46 V/cm Measurement Mode: Stationary 10 Cycles	Analysis Parameters Max Size: 100, Min Size: 10, Min Brightness: 20
1.05 0.9 0.8 0.7 0.6 0.5 0.5 0.4 0.5 0.4 0.5 0.5 0.4 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5	1.05 0.4 0.5 0.5 0.4 0.5 0.4 0.5 0.4 0.5 0.4 0.5 0.4 0.5 0.4 0.5 0.4 0.5 0.4 0.5 0.4 0.5 0.4 0.5 0.5 0.4 0.5 0.4 0.5 0.5 0.5 0.5 0.5 0.5 0.5 0.5
Stationary Layers Rel. Positior SL1 0.149 SL2 0.851	
Peak Analysis (25 ℃) Zeta Potential / mV Frequency FWHM / mV Percentage 1.3844 0.9924 7.4087 100.0000	
	Comment
	(Signati
Analyzed Video: C:\Users\zeta\Documents\ZetaData157UBC6June2013\20140311_0001_D	DA(Solid)-2X10-4M-pH 10.94_SL_comp.avi

Appendix 15: Zeta potential of DAH (solid) precipitate at pH 10.97







Appendix 17: Zeta potential of DAH precipitate at pH 10.87





Appendix 18: Zeta potential of DAH precipitate at pH 10.96



