School of Applied Chemistry

The Mechanisms of Action of Sodium Oxalate Seed Stabiliser Molecules under Bayer Conditions

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My stimulation:

When you reach for the stars, you may not quite get one, but you will not come up with a handful of mud either.

Leo Burnett

Certificate of Authenticity

The work described herein was performed by the author in the School of Applied Chemistry, Curtin University of Technology, Perth, WA; Alcoa World Alumina Australia, Kwinana, WA (Alcoa); CSIRO Minerals, Waterford, Perth, WA and University of Western Australia, Perth, WA from February 1996 to February 2000.

The work reported is (to the best of the author's knowledge) novel, and has not previously been submitted, in any form, for the purpose of obtaining any other degree or qualification. All work is that of the author alone, apart from that outlined below.

- All soluble sodium oxalate analysis and ICP measurements were performed by staff of Research & Development laboratory of Alcoa.
- Humic cake extract was isolated, supplied and its CMC determined by staff of Alcoa.

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Abbreviations

C10QA - decyltrimethylammonium bromide

C12QA - dodecyltrimethylammonium bromide

C13TA - tridecyldimethyl amine

C14QA - tetradecyltrimethylammonium bromide

C16QA - hexadecyltrimethylammonium bromide

C16EtQA - hexadecylethyl-dimethylammonium bromide

C16BenQA - hexadecylbenzyldimethylammonium bromide

C16PyrQA - hexadecylpyridinium chloride

C18QA - Octadecyltrimethylammonium bromide

CLSM - Confocal Laser Scanning Microscopy

CMC - critical micelle concentration

DBS - sodium dodecylbenzenesulfonate

DDACl - dodecyldecyldimethylammonium chloride

DiC16QA - dihexadecyldimethylammonium bromide

FTIR-ATR - Fourier Transform Infrared - Attenuated Total Reflection Spectroscopy

GC-FID - Gas Chromatography- Flame Ionization Detector

HAA - Humic acid from Aldrich

HAF - Humic acid from Fluka

LMW - Low Molecular Weight extract

MOST - Miniaturised Oxalate Stability Test

MOSPIT - Miniaturised Oxalate Seed Poison Impact Test

N138 - Oxalate stabilizer

N138# - Active content of oxalate stabilizer

OSP - Oxalate Seed Poisons

RSD% - Relative Standard Deviation Percentage

SDS - Sodium dodecylsulfate

TA or TAs - Tertiary amine or amines

TOC - Total Organic Carbon

QA or QAs - Quaternary amine or amines

Rationale

During the digestion of bauxite in caustic, and subsequent operations in a Bayer plant, entrained organic matter is degraded, much of it to the relatively stable oxalate anion. There is consequently a continuous build up of sodium oxalate in the Bayer liquor, and this must be removed in order to prevent unwanted crystallisation during hydrate precipitation. The solubility of sodium oxalate in Bayer liquors is quite low (ca 1 g/L), but the presence of other organic materials in the liquor can raise the precipitation threshold to in excess of 3-4 g/L. The relatively high oxalate solubility enables the plant to remove the oxalate less frequently, making the oxalate removal more economical. However, the stabilizing effects of these other organics are variable and unpredictable, and so synthetic molecules, that have very powerful stabilizing effects, are added. The earlier class of these molecules was anionic, but more recently formulations based on cationic quaternary amine salts have been found to be very effective.

From the large range of quaternary amine salts tested, an appreciation of the relationship of compound structure to liquor oxalate stabilization capacity has emerged. This structure-activity relationship has greatly assisted new product development, but the mechanisms by which additives worked were poorly understood. It was generally assumed that these molecules stabilized oxalate in solution by adsorbing onto oxalate nuclei, preventing their growth, but the mechanism was not known.

The overall aim of this work has been to investigate how quaternary amine salts affect the precipitation of sodium oxalate, and to understand the mechanisms, at a molecular level, by which specific additive molecules stabilize a high level of supersaturation of sodium oxalate in Bayer liquors in the presence of sodium oxalate seed. It was expected that this would lead to a better understanding of the adsorption of natural and synthetic organic compounds onto oxalate and the development of better stabilizer molecules. The following actions were planned to achieve this aim:

- Carry out literature and patent searches that relate to cationic surfactants and the mechanism of their adsorption onto substrates in general.
- Obtain quaternary amines of suitable purity that are similar to synthetic stabilizers used in industry.
- Classify quaternary amines as strong, medium or weak crystal growth inhibitors with a crystallization test in plant liquor.
- Measure the effect of selected quaternary amines on oxalate crystallization in synthetic liquor.
- Identify the features that are necessary for achieving a higher stabilization capacity of quaternary amines.
- Observe the nature of adsorption of additive molecules.
- Give a mechanism for the stabilization action of quaternary amines in Bayer liquor.

Abstract

Sodium oxalate is one of the many organics present in Bayer liquor. Due to its limited solubility, sodium oxalate can co-precipitate with alumina trihydrate during precipitation. This can have detrimental effects on the final product quality, especially if it occurs in the initial stages of precipitation.

Quaternary amine type cationic surfactants can prevent sodium oxalate co-precipitation and increase the tolerable concentration of sodium oxalate in Bayer liquor. Their action is via the inhibition of nucleation or/and the inhibition of crystal growth. This study presents work detailing the effect of quaternary amines on sodium oxalate crystal growth in Bayer liquor.

A series of quaternary amines were tested and classified as strong, medium or weak crystal growth inhibitors in plant liquor. The octadecyltrimethylammonium bromide was found to be the most effective under plant conditions.

Results will show that while quaternary amines inhibit crystal growth in Bayer liquor, they have no effect on crystallization in synthetic liquor. It has been postulated that the presence of certain organic molecules is required for quaternary amines to inhibit crystallization and therefore stabilize the liquor. The inhibition of oxalate crystal growth in Bayer process liquors is due to the plant organics present, and the stabilizing effect of quaternary amines is the result of an interaction between quaternary amines and plant humic material on the oxalate surface. A series of organics, anionic macromolecules and anionic surfactants, have been tested to simulate the behaviour of plant humates, and their inhibitory effect on sodium oxalate crystal growth has been measured.

A method for the analysis of the strongest quaternary amine has been adopted, improved and modified in order to fulfil experimental conditions.

The CMC of quaternary amines has been determined in liquor. Surface tension measurements revealed relationships between certain liquor components and quaternary amines.

Adsorption isotherms of quaternary amines have been successfully generated in Bayer liquor. Investigations with quaternary amines and plant humics reveal a

synergy between the two. Co-adsorption of quaternary amines and plant humates onto the oxalate surface has been found, and the effect of the components on the adsorption behaviour will be discussed. The inhibitory effect and the adsorbed amount of components have been compared. Results revealed a relationship between the amount of plant humates on the surface and the crystal growth inhibition.

The nature of the adsorption has been investigated with confocal laser scanning microscopy. These results will show that humic material adsorbs at the edges and in the corners of the crystals. In the presence of quaternary amines, the humic material occupies the main crystal faces as well. The nucleation of sodium oxalate from humic solution and from a mixture of humates and quaternary amine resulted in crystals with different morphology.

Fourier Transform Infrared Attenuated Total Reflection Spectroscopy investigations will present the adsorption of quaternary amine on oxalate, and will indicate that the adsorption is pH dependent.

Chapter 1

Introduction

1.1 The Bayer process

The Bayer Process as we know it today involves four main steps:

- The pressure leaching of bauxite with NaOH solution to obtain sodium aluminate solution.
- Red mud/undissolved residue separation
- The precipitation of pure aluminium hydroxide from this solution by seeding with fine crystals of $Al_2O_3*3H_2O$, alumina trihydrate.
- The calcination of alumina trihydrate to anhydrous alumina.

In 1888 a British Patent entitled " A Process for the Production of Aluminum Hydroxide" was issued to the Austrian chemist Karl Josef Bayer. At that time Bayer's invention was to satisfy the need of the Russian textile manufacturers. Soon, it turned out to become the most important invention for supplying the need of the growing electrolytic aluminium industry discovered by Hall and Heroult.

The modern industry is still in the process of growth. The aluminium production of the world is approximately 22 megatonnes a year, which involves the production of 47 megatonnes of alumina every year. Australia is the world's largest producer of alumina and the largest refiner of bauxite. Almost 30 % of the world's production of alumina comes from Australia. Australia holds estimated bauxite stocks of over half a billion tonnes, which indicates a magnificent prospect for an ongoing existence of aluminium industry in this region (Hind, Bhargava & Grocott 1999).

1.1.1 Bauxite

Alumina is produced from bauxite all over the world. Bauxite refers to an ore or mixture of minerals rich in aluminium. The aluminium occurs in bauxite as gibbsite ($Al_2O_3*3H_2O$, alumina trihydrate), and as bömite and diaspore, two forms of

monohydrate (Al(OH)O). The hydrated alumina in bauxite is accompanied by various impurities derived from the parent rocks. Due to the alkaline leaching, the main impurities getting into the process are: silicon, iron, titanium, calcium, carbon, chromium, gallium, fluorine, beryllium, magnesium, niobium, phosphorus, potassium, rare earth elements, vanadium, zinc and zirconium in different forms. These impurities affect the production and the quality of alumina and the final product, the aluminium. Although, the chemical principles of the Bayer process have not changed much (Pearson 1955), the physical nature of the bauxite (clay-like, rock) and the necessity of removal of impurities originating from the actual bauxite determine the design and the structure of an alumina refinery.

1.1.2 The industrial operation

The Bayer process practically is the process of re-crystallization of the aluminium hydrate from bauxite. The process can be represented by three equations:

Extraction

$$Al(OH)_3 + NaOH \rightarrow Na^+ + Al[(OH)_4]^- \quad \text{or}$$

$$Al(OH)O + H_2O + NaOH \rightarrow Na^+ + Al[(OH)_4]^- \qquad (1.1)$$

Precipitation

$$Al[(OH)_4]^- \rightarrow Al(OH)_3 + OH^- \qquad (1.2)$$

Calcination

$$2\ Al(OH)_3 \rightarrow Al_2O_3 + 3\ H_2O \qquad (1.3)$$

The bauxite is first digested with hot caustic soda solution, usually under pressure. The aluminium hydrate is extracted in the form of soluble sodium tetrahydroxo-aluminate (1.1), which leaves behind most of the impurities, predominantly iron oxide, titanium oxide and silica, as an insoluble residue. The clear, filtered sodium tetrahydroxo-aluminate solution is diluted and cooled, and a seed of alumina trihydrate is added. The tetrahydroxo-aluminate releases a hydroxide ion on the surface of the seed to form crystalline alumina trihydrate (1.2). The trihydrate is finally filtered off and calcined to anhydrous alumina (1.3). Then, the spent liquor is concentrated, heated and fed back to the onset of the process. Figure 1.1 shows the flowsheet of the Bayer process.

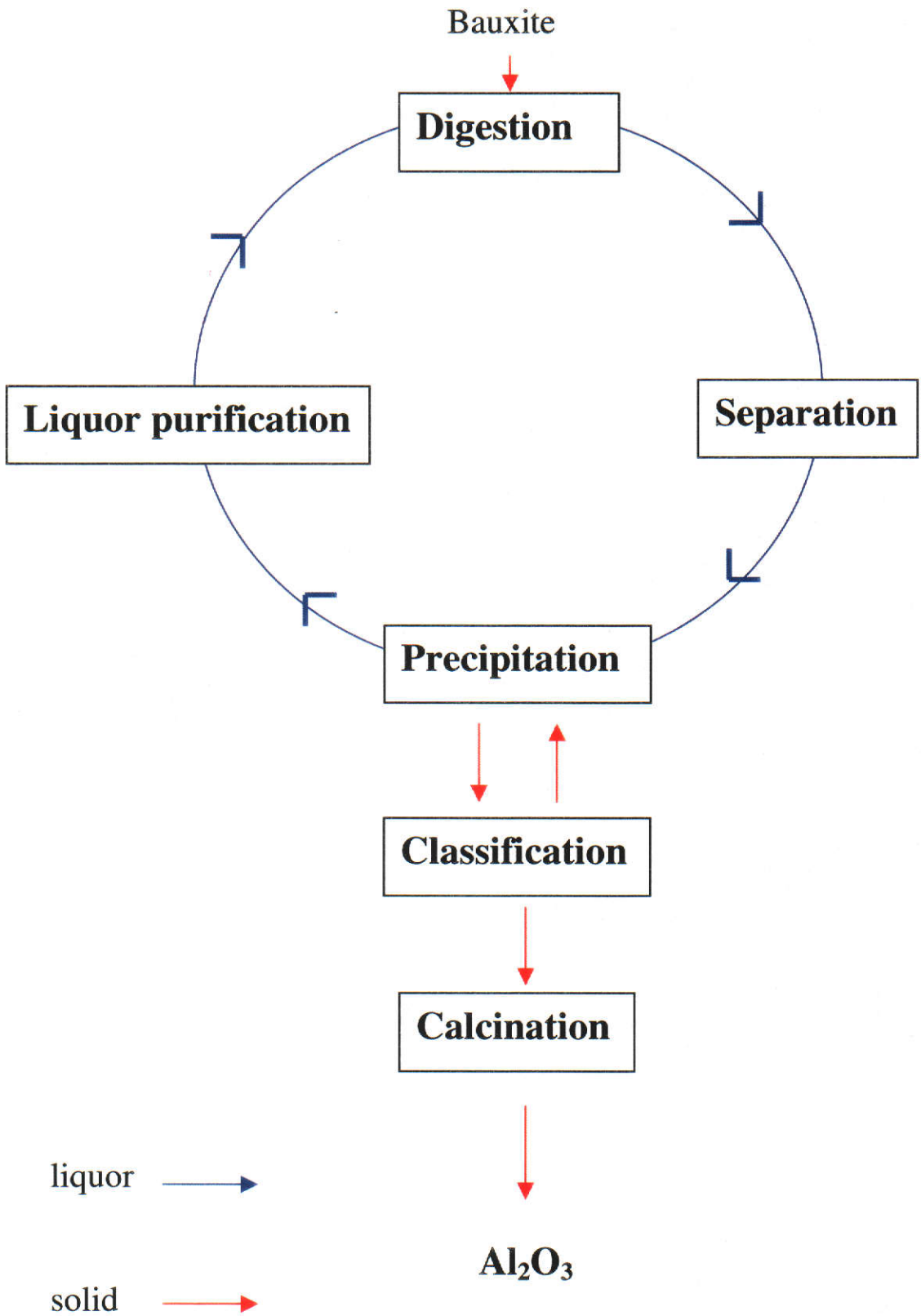

Figure 1.1: Flow sheet of simple Bayer process containing oxalate removal (liquor purification)

1.1.3 Sodium oxalate in the Bayer process

Most bauxites contain organic matter in various amounts. The major source of organic matter that is introduced into the Bayer liquor is from the bauxite in the form of humic substances. During the digestion, the organic matter is dissolved, degraded and oxidised with the results that the liquors darken, and notable amounts of oxalate and carbonate are formed.

Due to the acidic nature of the humic substances, more than 50% of the organic matter contained in the bauxite is extracted into the liquor. The principal degradation products are sodium oxalate and sodium carbonate. Depending upon the digestion conditions, typically 5-10 % of the organic carbon is converted to sodium oxalate. Australian bauxites have conversion rates of two or three times higher (Lever 1983; Grocott 1988).

In the Bayer process the caustic liquor is recycled, and because of this the organic matter builds up to an equilibrium level, typically to 10-30 g/L of organic carbon content, determined by the outputs and the inputs (Gnyra and Lever 1979). Beside the bauxite input, some organic matter come from other sources, such as process water, grease, red mud flocculants or antifoams. The outputs are through the adsorption on the red mud, or degradation to smaller molecular weight organics and carbonate or adsorption on the product gibbsite.

In the conventional Bayer process, there is no outlet for the sodium oxalate, except some losses on the red mud. The sodium oxalate, if not controlled, builds up to a certain level of supersaturation, and precipitates out as fine needles in cooler parts of the circuit. It may co-precipitate with the hydrate product causing productivity, operational and maintenance problems. For this reason, most refineries apply oxalate removal in one way or another.

1.1.4 Effect of sodium oxalate co-precipitation with gibbsite

Sodium oxalate has been shown to be very harmful with regard to alumina productivity and size (Calalo and Tran 1993; Brown and Cole 1980). When sodium oxalate, if not controlled, builds up to a certain level of supersaturation, it precipitates

out as fine needles in the hydrate precipitator tank. This co-precipitation affects the alumina product quality and the productivity in many ways:

- Trihydrate production is often limited by processing conditions that are determined by oxalate solubility.
- High quality aluminium trihydrate has a coarseness of crystals being at least 44 microns in diameter (Farquharson *et a.*, 1995a). The oxalate needles act as nuclei for hydrate precipitation and give rise to hydrate fines.
- Gibbsite particle size enlargement occurs via the agglomeration and the crystal growth of hydrate. The presence of oxalate causes nucleation to dominate agglomeration thus reducing agglomeration efficiency.
- The presence of crystalline sodium oxalate (that decomposes at 450 °C) with the hydrate crystal reduces product particle size during calcination.
- The amount of incorporated sodium oxalate varies in the product hydrate causing problems in the smelting of alumina to aluminium. It becomes difficult to balance the soda input.
- Oxalate precipitation results in soda loss that increases the overall expenses.
- The attachment of oxalate to alumina trihydrate interferes with particle size classification.

Due to the tremendous effects of sodium oxalate co-precipitation on alumina quality and productivity, it is necessary to analyse, forecast and control the dissolved sodium oxalate concentration in plant process liquors of high organic content (Grocott 1988).

1.1.5 Oxalate removal processes

As the oxalate concentration builds up in the liquor, it has to be precipitated. Different refineries adopt different removal processes.

Some refineries let the sodium oxalate co-precipitate with gibbsite in the growth phase. Then, the gibbsite is washed free of solid sodium oxalate with water.

Other refineries crystallize sodium oxalate in a separate crystallizer. The liquor is usually cooled and evaporated, then, seeded with sodium oxalate crystals. The resulting oxalate cake is filtered. Refineries operating an oxalate crystallizer avoid co-precipitation of oxalate with gibbsite.

The oxalate cake can be burnt in a solid-liquid calciner to recover caustic or consumed by bacteria in a specially designed pond. Very often, the oxalate cake or the wash water rich in oxalate is disposed of.

1.1.6 Solubility of sodium oxalate in Bayer liquors

It is well known that increasing caustic levels and decreasing precipitation temperatures generally decrease the solubility of sodium oxalate in Bayer process liquor. However, to obtain the maximum recovery of alumina hydrate from Bayer process liquor, a plant will typically attempt to maximise the liquor caustic level and minimise the final precipitation temperature. Therefore, the plant operates under conditions where the dissolved sodium oxalate concentration is very close to its solubility limit. Many publications found in the literature deal with oxalate solubility and parameters affecting oxalate solubility (Beckham and Grocott 1993; Bouzat and Phillipponneau 1991; The and Bush 1987; Lever 1983; Brown and Cole 1980).

The thermodynamic solubility of sodium oxalate in Bayer liquors is quite low (ca 1 g/L), depending on the temperature and the caustic concentration. However, the presence of other organic materials, mainly high molecular weight humic substances, in the liquor can raise the precipitation threshold to in excess of 3-4 g/L (Lever 1981; Lever 1983). This apparent solubility is termed the critical oxalate concentration (COC), or the oxalate stability of liquor. While the solubility of oxalate is a thermodynamic parameter, the stability of oxalate refers to a time-dependent apparent oxalate solubility. Unfortunately, the stabilizing effects of the organic matter in process liquors are variable and unpredictable.

1.1.7 The effect of high molecular weight organics

The organic matter in the Bayer process liquors consists mainly of a complex mixture of:

a) high molecular weight humic substances
b) intermediate molecular weight benzene carboxylic, phenolic and hydroxy aliphatic acids
c) low molecular weight carboxylic and hydroxy carboxylic acids (Lever 1978).

It has been shown that the high molecular weight humic compounds are responsible for a series of effects (Wilson *et al.* 1998; Norman *et al.* 1997; Singer and Huang 1990). The role of other organics has not been clarified.

The humic substances present at high concentrations adsorb on the hydrate causing colouration of the crystals, deactivate the seed and increase liquor stability with respect to alumina trihydrate and result in caustic loss.

The adsorption of humic material on oxalate seed increases the oxalate stability; this is beneficial during hydrate precipitation, but inhibits oxalate removal (Lever 1983). The dramatic effect of plant humates on oxalate morphology has been shown previously (Brown 1988).

Due to their surfactant nature, humic substances are responsible for liquor foaming and interference with red mud flocculation.

1.1.8 Methods for sodium oxalate control in the Bayer process

The operational requirements for oxalate stability are different in different areas of the Bayer circuit. In Alcoa refineries it is desirable to have a high dissolved oxalate concentration tolerated during the entire process of hydrate precipitation, whilst a low stability is required during oxalate removal to make the removal as efficient as possible.

It has been shown that the removal of a small fraction of the high molecular weight humates from the Bayer process liquors destabilizes the dissolved sodium oxalate and results in its spontaneous crystallization (Lever 1981; Atkins and Grocott 1993). Several methods of overcoming the stabilizing effect of these high molecular weight humates have been patented. U.S. Patent 3,337,305 (Byrns 1976) describes a method in which sodium oxalate is precipitated from solution by the addition of aqueous ammonia. In U.S. Patent 3,649,185 (Sato 1972), sodium oxalate precipitation is affected by the addition of NaOH, thus decreasing the solubility of sodium oxalate. U.S. Patent 3,899,571 (Yamada 1975) discloses a method in which seeding with activated crystals of sodium oxalate stimulates precipitation.

Some of the patents disclose methods that target directly the removal of high molecular weight organics responsible for the stabilising effect of sodium oxalate. U. S. Patent 3,457,032 (Breteque 1969) describes a method involving passing Bayer

liquor through a bed of a strongly basic anion exchange resin to eliminate organic impurities. U.S. Patent 4,275,042 (Lever 1981) is about the removal of sodium oxalate from supersaturated solution of Bayer spent liquor by the treatment with cationic sequestrants. U. S. Patent 4,275,043 (Gnyra 1981) refers to similar treatment through the use of activated carbon and U.S patent 4,578,255 gives a method for the purification of the liquor by the addition of vinylic cationic polymeric quaternary ammonium salts (Roe and Malito 1986).

There are already two patents registered about the stabilising effect of synthetic organics. Cationic surfactants can be used to stabilise sodium oxalate further in Bayer process liquors. U. S. Patent 5,385,586 (Farquharson *et al.* 1995b) refers to a method for inhibiting the precipitation of sodium oxalate by the addition of an alkylammonium salt. AU Patent AU9733241 (Farquharson and Kildea 1998) describes a process using a mixture of surfactants to achieve high dissolved oxalate concentrations.

1.1.9 Synthetic stabilizers

Stabilization of sodium oxalate in solution controls the productivity of many refineries. An increase in the dissolved oxalate concentration tolerated during hydrate precipitation will allow an increase of caustic concentration and a decrease in precipitation temperature without the co-precipitation of sodium oxalate. This, in turn, increases the productivity and improves the classification of hydrate.

A number of compounds such as humic acids and some anionic polyelectrolytes have been previously identified to increase the stability of sodium oxalate in Bayer liquors (Lever 1983). However, a chemical that increases oxalate stability has no use unless it can be removed or destroyed before the oxalate removal circuit (section 1.1.2).

Quaternary amine salts have been found to be very powerful oxalate stabilizers in Bayer liquors (Farquharson *et al.* 1995a; Farquharson *et al.* 1995b; Farquharson *at al.* 1996). Synthetic stabilizers are added into the Bayer process liquor after red mud separation prior to precipitation of alumina trihydrate. And, they are thermally inactivated when the liquor is recycled to the digestion step where the liquor is

heated up to a temperature of at least about 130 °C. The degradation products, amines and alkenes, have no downstream side effects in the Bayer process.

From the wide range of quaternary amine salts tested, an appreciation of the relationship of compound structure to liquor oxalate stabilization capacity has emerged. This structure-activity relationship has greatly assisted new product development, but the mechanism by which these additives work is poorly understood (Farquharson 1996).

1.2 Crystal growth

The liquor is seeded in both the hydrate precipitation and oxalate removal circuits of the Bayer process (section 1.1.2). Efficient filtration and suitable handling properties require a certain size and size-distribution of hydrate and oxalate crystals. The control of the size of crystals is achieved by careful classification and preparation of seed followed by enlargement processes under conditions avoiding unwanted primary nucleation. Although agglomeration is an important enlargement process for hydrate, the favoured enlargement route is crystal growth for both the hydrate and sodium oxalate solids.

1.2.1. Supersaturation and crystal growth rate

When the concentration of a component is above its solubility in a solution, the system is supersaturated with respect to the component at a given temperature (Myerson 1993; Mullin 1993). The supersaturation can be expressed by **S**, the supersaturation ratio, which is the ratio of the actual concentration (**C**) and the solubility of the component (**C***):

$$S = \frac{C}{C^*} \tag{1.2.1}$$

or by the difference of these two concentrations:

$$\Delta C = C - C^* \tag{1.2.2}$$

or by the relative supersaturation, σ:

$$\sigma = \frac{C - C^*}{C^*} \tag{1.2.3}$$

When seed crystals are added into a supersaturated system, they begin to grow into bigger crystals. The overall crystal growth rate at a given temperature can be expressed as a mass deposition rate, $\mathbf{R_G}$:

$$R_G = k\sigma^a = \alpha \frac{dm}{dt} \tag{1.2.4}$$

where **k** and α are rate coefficients, **a** is the growth order depending on the surface area, shape and size of the crystals, and **m** is the mass. The mean linear velocity is explained by the following equation:

$$R_G = k\sigma^a = \beta \frac{dL}{dt} \tag{1.2.5}$$

or the overall linear growth rate is given by

$$R_G = k\sigma^a = \gamma \frac{dr}{dt} \tag{1.2.6}$$

where **L** is a characteristic size of the crystal, **r** is the radius corresponding to the equivalent sphere, and β and γ are constants.

A number of theories for mechanisms of crystal growth have been proposed.

1.2.2.Crystal growth theories

Surface energy theories

These theories are based on the minimum surface free energy principle of Gibbs, originally established for fluid droplets. According to this principle, the crystals grow in a supersaturated solution to develop an equilibrium shape in which the crystals have a minimum total surface free energy for a given volume. Although these theories have a limited capacity to explain the effect of parameters on the growth kinetics, they are useful in treatments that relate the free energies of faces to their rates of growth.

Adsorption layer theories

These theories are built on the following thermodynamic treatment given by Gibbs and Volmer. When crystal units arrive at the crystal face, they develop a loosely adsorbed layer having lost one degree of freedom. These units can migrate over the crystal face, and get integrated into the lattice in positions where the attractive forces are greatest. This build-up creates a step-wise development, and it continues until the whole plane is completed. Then, a new two-dimensional nucleus is formed on the surface and a further layer commences. The units in the adsorbed layer are in equilibrium with those in the bulk.

Kinematic theories

The adsorption layer theories predict the development of moving layers (steps) of monoatomic height on the crystal surface. Kinematic theories describe crystal growth with density of steps (the number of steps per unit length in a given region) and step flux (the number of steps passing a given point per unit time).

Diffusion-reaction theories

Diffusion theories consider that the deposition of solid on the face of a growing crystal is a process controlled by diffusion. The driving force for crystal growth is the difference between concentrations at the solid surface and in the bulk solution. The theories allow the existence of a stagnant film of liquid on the surface. There are two steps in the mass deposition, the transport of molecules to the surface film and a surface reaction when the solute molecules arrange themselves into the crystal lattice. The diffusion theory can not explain the mechanism of growth, like layer growth; however, the mass transfer can be given conveniently by its mathematical expressions.

Birth and spread models

These models are based on crystal surface nucleation followed by the spread of the monolayer. Surface nucleation can occur at the edges, corners and on the faces of a crystal. Further surface nuclei develop on the monolayer as they spread across the

crystal face. The significance of these models developed in recent years is that they describe the crystal growth allowing growth orders greater than 2.

1.2.3 Parameters affecting the rate of crystal growth

Temperature

The relationship between a reaction rate constant, **k**, and the absolute temperature, **T**, is given by the Arrhenius equation

$$\frac{d\ln k}{dT} = \frac{E}{RT^2} \quad \text{or} \quad \frac{d\ln k}{d(1/T)} = -\frac{E}{R} \tag{1.2.7}$$

where **E** is the energy of activation and **R** is gas constant. Activation energies are usually positive. With increasing temperature, the rate coefficient and the rate of crystal growth are increased at a given supersaturation.

Crystal size

Crystal growth rates can be particle-size dependent. This effect can originate from three sources.

1) Small crystals have higher solubility due to the Gibbs-Thomson effect. Therefore they experience lower supersaturation and slower growth rate than the bigger crystals.
2) Small crystals have a small terminal velocity and they may be growing in a stagnant medium, even in a well-agitated system. Big crystals have a higher velocity compared to the solution velocity, therefore they grow faster in systems where the control process is the transport of solute molecules to the surface.
3) The number of dislocations in a crystal increases with size due to mechanical stresses, energetic collisions, etc. These effects favour faster surface integration kinetics and lead to higher growth rates with increasing crystal size.

Growth rate dispersion

Growth rate dispersion refers to the fact that individual crystals, all initially of the same size, can grow at different rates, due to internal differences (eg defect content, impurities, etc) and to their different growth environment (eg temperature, supersaturation, hydrodynamics, etc).

Additives

The effect of additives is variable. Some additives suppress crystal growth rate, and some may enhance it. Others modify the crystal morphology by acting on specific faces of crystals.

Additives can influence crystal growth rates in many ways. They can

a) change the properties of the solution (increase boiling point, viscosity, change colour)
b) alter the equilibrium solubility and hence change the supersaturation
c) alter the characteristic of the adsorption layer at the crystal-solution interface
d) be built into the crystal
e) adsorb selectively onto different crystal faces

Crystal growth retardants, like stabilizers of Bayer solids, often adsorb onto faces of crystals and retard their growth rates. Selective adsorption onto different faces often results in modification of morphology.

1.2.4 Growth and growth inhibition of oxalates

Calcium oxalate is the most investigated solid oxalate in the literature. Calcium oxalate is the principal crystalline component of over 90% of human urinary stones. In this calcific deposit, inorganic crystals are mixed with an organic matrix of urinary macromolecules that includes proteins, lipids and carbohydrates. In the kidney, oxalate and phosphate are concentrated, resulting in supersaturation with respect to their calcium salts. Heterogenous precipitation is normal, and in non-stone formers the effects are minimized by the production of protein and small molecule inhibitors. In stone-formers, it is often found that the production of inhibitors is

unusually small, or that there are high levels of nucleation promoters. Among the promoters are acidic phospholipids that have been shown to catalyse calcium oxalate precipitation (Whipps *et al.*1998). The interactions between the phospholipid molecules and stone crystals have been studied (Backov *et al.*2000).

In contrast to most of crystallization studies, the interest on calcium oxalate crystal growth is oriented to suppress it. The existence of natural inhibitors in urine has been recognised and components such as citrate, phytate (Millan, Sohnel & Grases 1997; Grases & March 1898) magnesium, pyrophosphates, serum albumin (Smesko *et al.* 1988), amino acids (Fleming, Bronswijk & Ryall 2001), polysulphates (Grases, Gil & Conte 1989; Linder & Little 1986) have been studied. These studies in agreement with some other investigations aiming at the control of phase transformation of calcium oxalate (Tunic *et al.* 1996: Tunic *et al.* 1998) demonstrate that the kinetics of precipitation of calcium monohydrate is surface reaction controlled. The rate order of calcium oxalate monohydrate precipitation was 2 in all cases suggesting a spiral growth mechanism.

Calcium oxalate is also investigated as a model system because it crystallizes from aqueous solution in the form of three different hydrates with different crystallization kinetics. The composition of the crystallizing phase can be controlled by additives (Tunic *et al.* 1996: Tunic *et al.* 1998). The morphologies show a variety and are influenced by macromolecules in natural formations such as plants (Bouropoulos, Weiner & Addadi 2001)

Sodium oxalate is a semi-soluble salt in Bayer liquor. The lack of studies investigating sodium oxalate in solution of low ionic strength is probably due to its high solubility in water.

1.3 Adsorption

1.3.1 Adsorption process

Bayer organics (section 1.1.6) and synthetic stabilizers (section 1.1.8) adsorb onto the surface of the Bayer solids, alumina trihydrate and sodium oxalate. As a result of the adsorption, these chemicals retard the crystal growth of hydrate and oxalate, causing their stabilization in solution.

Adsorption refers to the accumulation of a matter at the interface. The adsorption can be physical (reversible) or chemical (irreversible). For the adsorption process,

$$A + S \leftrightharpoons AS \tag{1.3.1}$$

the mass action law is given by

$$K = \frac{[AS]}{[A][S]} \tag{1.3.2}$$

where **A** refers to the adsorbate and **[A]** represents its concentration (activity) in solution (mol dm^{-3}), **S** refers to the surface site of adsorbent (adsorption sites) and **[S]** is its concentration (mol m^{-2}), **AS** represents the adsorbate on the surface site and **[AS]** is its surface concentration (mol m^{-2}). **K** is the equilibrium constant of the adsorption process at a given temperature.

1.3.2 Adsorption isotherms

Adsorption isotherms relate the bulk concentration (activity) of adsorbate to the amount adsorbed on the surface. Adsorption isotherms reflect equilibrium conditions.

The simplest adsorption isotherm shows linear relationship between the surface concentration **[AS]** and concentration (activity) of adsorbate **[A]** in solution. This linear relationship is commonly referred to as Henry's law:

$$[AS] = K[A] \tag{1.3.3}$$

Adsorption isotherms, different from the one above, can be classified into five classes (Ruthven 1984: Basmadjian 1997). The most commonly used isotherms are the Langmuir and the Frumkin type isotherms in solutions.

The Langmuir isotherm represents type I isotherms, and describes a monolayer adsorption in the form of

$$[AS] = S_{max} \frac{K[A]}{1 + K[A]} \tag{1.3.4}$$

where $\mathbf{S_{max}}$ defines the maximum concentration of surface sites, the adsorption capacity and **K**, the equilibrium constant is called as the adsorption affinity.

1.4 Surfactants

1.4.1 Introduction

The production of alumina trihydrate is directly limited by the stability of sodium oxalate in the Bayer process. However, the organic matter naturally occurring in the process liquor or the addition of synthetic stabilizers can influence the oxalate stability. In Alcoa's laboratories, research has commenced to clarify the exact nature and role of the components of the organic substances. The work being reported here is about the effect of synthetic stabilizers on oxalate crystallization.

The organic matter in Bayer liquors is not a uniform compound. It consists of a complex mixture of surfactants and polyelectrolytes of surfactant nature (section 1.1.6). The synthetic stabilizers developed recently belong to the class of surfactants as well. It seems that surfactant type compounds play an important role in the Bayer process. The surface chemistry of these surfactants determines the efficiency of many refineries.

1.4.2 Classification of surfactants

Surfactants are organic molecules that contain two functionalities with different characteristics. A surfactant contains both a hydrophilic (water-soluble) polar portion and a hydrophobic (water-insoluble) non-polar portion. They are classified into two broad classes and five subclasses as follows (Rubingh and Holland 1991):

Ionic class

- Anionic subclass
- Cationic subclass

Nonionic class

- Zwitterionic subclass
- Semipolar subclass
- Single-bond subclass

It is helpful to state here that the naturally occurring surfactants of the liquor belong to the anionic class, and all of the synthetic stabilizers are cationic surfactants.

1.4.3 Micellization of cationic surfactants

When cationic surfactants are dissolved in water or non-aqueous solvents, they behave like electrolytes. The solution contains free surfactant cations ($\mathbf{A^+}$) and counterions ($\mathbf{X^-}$). Micellization refers to a process when aggregates of surfactants start forming in solution:

$$nA^+ + mX^- \leftrightharpoons A_nX_m^{(n-m)+} \tag{1.4.1}$$

where **n** is the micelle mean aggregation number and **(n-m)** is the degree of micelle ionization. The concentration of surfactant at which the micelle formation commences is termed the critical micelle concentration (CMC). The equilibrium constant, **K** for reaction (1.4.1) is given by

$$K = \frac{[A_nX_m]}{[A^+]^n[X^-]^m} \tag{1.4.2}$$

where the bracketed quantities refer to activities. A similar treatment can be applied for anionic surfactants. The equation can interpret the characteristics of a surfactant solution above its CMC. Due to the exponential expression of $\mathbf{A^+}$ in equation (1.4.2), the concentration of free surfactant cations remains constant with increasing surfactant concentrations; only, the concentration of micelles increases.

All characteristics of a surfactant solution undergo changes upon micellization. The onset of micellization, the CMC, can be affected by various parameters. Increasing temperature and surfactant chain length result in the decrease of the CMC. The nature of the counterion determines the CMC as well. The larger and more polarizable the counterion, the smaller the CMC.

Increasing ionic strength decreases the CMC for a given counterion. It should be noted that surfactant solutions might become non-idealistic at high ionic strength. The micelle formation can be continuous, starting with small mean aggregation numbers and developing huge aggregates at high concentrations. The shape of micelles might alter as well.

1.4.4 Adsorption of surfactants at the liquid-air interface

When surfactants are dissolved or dispersed in water or non-aqueous solvents, the molecules will orient themselves in specific ways at the interface of the liquid-air

or of the solid-liquid. This orientation of the molecules changes the surface properties of the system at the interface.

Adsorption of cationic surfactants at the liquid-air interface is not as commercially important as adsorption at the solid-liquid interface. Foaming and emulsifications are the two most important practical applications. Another application is the commercial detergents and cleaning agents.

Recently, a new technique, the neutron reflection technique was developed for studying adsorption of surfactants at the liquid-air interface. This method can provide much information about the structure of adsorption layer (Eastoe *et al.* 1996).

The quantitative adsorption of a surfactant at a liquid-air interface is usually investigated by measuring the surface or interfacial tension (surface tension isotherms). The tension falls with increasing surfactant concentration, and becomes almost constant above the critical micelle concentration. The tension measurement is relatively simple compared to direct measurement of adsorption. The techniques commonly used include the maximum bubble pressure method (Yaminsky, Ninham & Stewart 1996), the du Noüy ring maximum force method (Furlong *et al.* 1983), the drop volume method and the Wilhelmy plate method. In this study, the Wilhelmy plate method has been chosen to determine the CMC of surfactants. The weight of a glass slide was measured prior to making contact and in perpendicular contact with the liquor surface. The decrease in weight of the glass slide is directly proportional to the surface potential (surface tension) at the liquor-air interface. The CMC of a surfactant can be determined from a plot of surface tension versus surfactant concentration. The intersection of two straight lines drawn through data points obtained at concentrations of surfactant below and above the CMC determines the CMC. Figure 1.2 shows the CMC of C18QA determined in liquor at 60 °C with the method described.

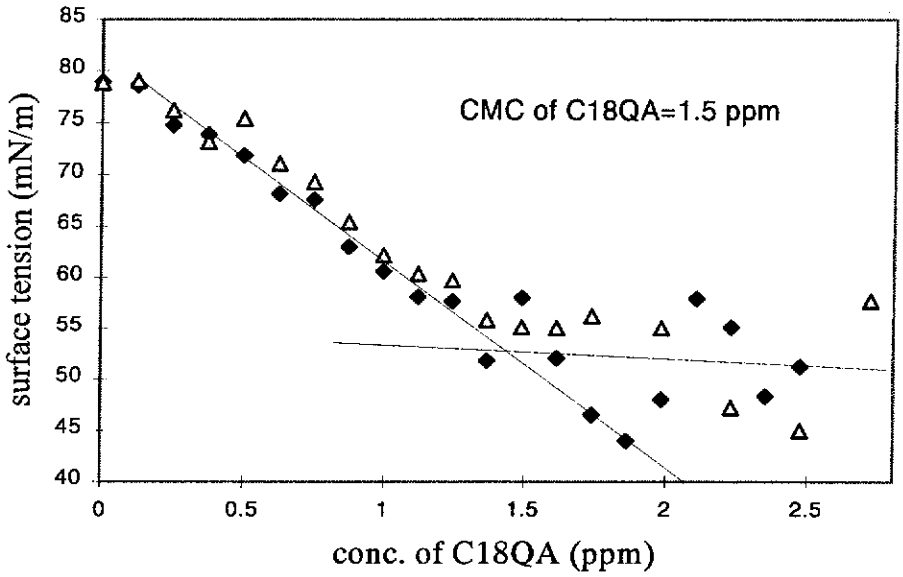

Figure 1.2: The surface tension of synthetic liquor as the function of C18QA concentration at 60 °C. The CMC of C18QA determined from data is 1.5 ppm. Duplicate measurements.

The surface tension curve of a surfactant is very often used as a calibration curve at concentrations below the CMC. This enables adsorption measurements on solids for surfactants that cannot be quantified with other analytical methods (Paxton 1969; Ivanova, Volchkova & Schhukin 1995; Zhao and Brown 1995; Zhao and Brown 1996).

1.4.5 Adsorption of surfactants at the solid-liquid interface; Adsorbents

Adsorption of surfactants, reported in the literature, involves a wide variety of adsorbents. Adsorbents can be classified based on their nature (Rubingh and Holland 1991):

- uncharged hydrophobic surfaces (graphite, wax, polymers)
- charged hydrophobic surfaces (silica, polymers with relatively low surface charge density)
- charged oleophobic surfaces (PTFE)
- hydrophilic surfaces (cotton, protein)
- low charged hydrophilic surfaces (surfaces just above the isoelectric point)
- highly charged hydrophilic surfaces (clays and minerals).

Crystalline solids can be considered as hydrophobic surfaces with charged sites. The lattice ions are the potential determining ions. Thus, the surface charge is positive in the excess of cations, and negative in the excess of anions.

A number of studies have been reported in which surfactants adsorb on crystalline solids. However, oxalate salts have attracted little interest in surfactant adsorption. Only one publication is reported about the adsorption of cationic dodecyldimethylammonium chloride (DDACl) and anionic (SDS) surfactants on calcium oxalate (Škrtić *et al.* 1993). Sodium oxalate, as adsorbent, has become the matter of interest recently in connection with synthetic stabilizers (Hind, Bhargava & Grocott 1997). The study deals with quaternary amine adsorption on sodium oxalate from solution of high ionic strength (5M NaCl) and of high pH (12). The authors investigated quaternary amine adsorption using FTIR/ATR; and concluded that quaternary amines adsorb on the oxalate surface from solution of pH 12 in the presence of plant organics. Adsorption – dose response curves were obtained for C12QA, C14QA and C16QA.

Sodium oxalate is a semi-soluble salt in Bayer liquor. The lack of studies investigating adsorption on sodium oxalate from solution of low ionic strength is probably due to its high solubility in water.

Sodium oxalate substrate can be produced from water, resulting in blocky oxalate crystals that are usually highly aggregated. From basic solution, needle-like, acicular crystals can be obtained. The work reported here was done with acicular sodium oxalate.

1.4.6 Adsorption of surfactants at the solid-liquid interface; Adsorption models

Adsorption of surfactants on mineral surfaces has been studied intensively, being a topic of both practical and academic interest. Classic model surfaces for adsorption of cationic surfactants are negative silicas (Ghosh *et al.* 1995; Goloub *et al.* 1996; Zajac, Trompette & Partyka 1996). The adsorption of anionic surfactants is mostly studied on positive metal oxide surfaces such as rutile or alumina (Lee and Koopal 1996; Koopal, Lee & Bohmer 1995; Couzis and Gulari 1993). However, the adsorption of surfactants is not restricted by the opposite charge of the surface. Both

cationic and anionic surfactants can adsorb onto surfaces under the same conditions (Škrtić *et al.* 1993).

Interpretation of the adsorption mechanism has often been based on the shape of the adsorption isotherm (Wängnerud, Berling & Olofsson 1995; Koopal, Lee & Bohmer 1995; Zhao and Brown 1996). The shape of the isotherms will vary considerably with the chosen mode of representation. Cationic and anionic surfactant adsorption on surfaces mentioned above at low ionic strength shows a two-step shape in a linear-linear plot, and a four – region adsorption isotherm in a log-log plot (Figure 1.4).

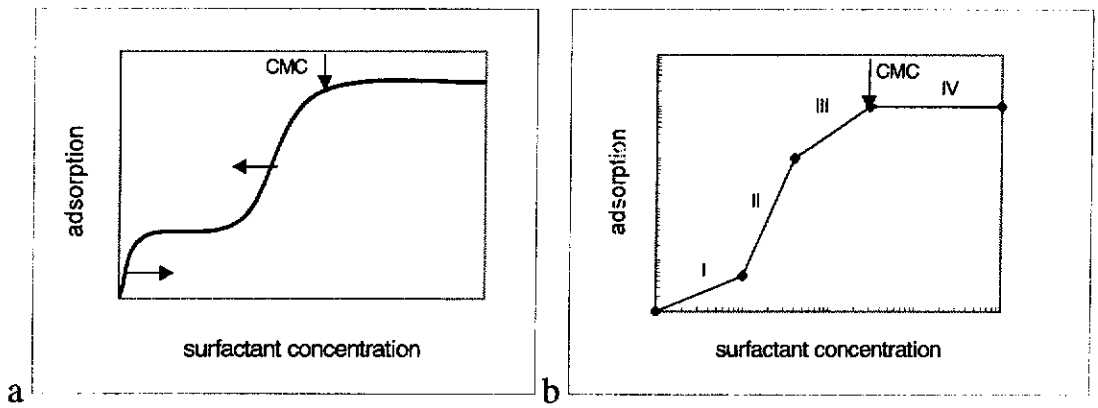

Figure 1.4: General shape of adsorption isotherm of surfactant in a (a) linear-linear plot, and (b) in a log-log plot at low ionic strength. The arrows indicate the influence of increasing ionic strength.

In the isotherm shown in Figure 1.4a, a small amount of surfactant adsorbs onto the solid surface at low surfactant concentration. This adsorption is due to the electrostatic attraction between the charged head group of the surfactant and the opposite charge on the solid surface. This is depicted as region I in Figure 1.4b. At these low concentrations, there is no interaction between the surfactant molecules either in solution or on the solid surface. As the charged sites at the surface become occupied by surfactant ions, the slope of the isotherm decreases, and the first plateau develops.

As the concentration of surfactant molecules increases, the spacing between the adsorbed molecules decreases. Eventually, the spacing is sufficiently small to allow interaction between the hydrophobic tails of the surfactants. At this point, a rapid

increase in surface adsorption occurs (region II in Figure 1.4b). In this region, hemi-micelles, defined as aggregates of "head-on" adsorbed surfactant ions, are formed. In region III, the hemi-micelles transform into ad-micelles, defined as aggregates of both "head-on" and "head-out" adsorbed surfactant ions. Adsorption beyond the monolayer requires that the attraction between the hydrophobic surfactant tails is greater than the electrostatic repulsion between the head groups.

Region IV in Figure 1.4b occurs once the CMC is reached. When the surfactant concentration reaches the CMC, the concentration of free surfactant in solution becomes constant. This is the second plateau in Figure 1.4a.

Adsorption of surfactants depends on a number of factors such as temperature, surface character, pH of solution, ionic strength, electrolyte composition and the molecular structure of surfactants. At high ionic strength, the shape of the adsorption isotherm is altered (Figure 1.5).

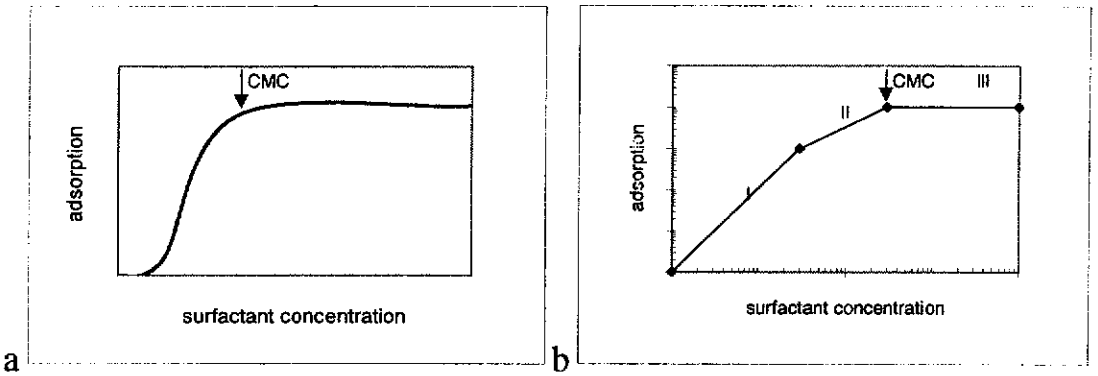

Figure 1.5: General shape of adsorption isotherm of surfactant in a (a) linear-linear plot, and (b) in a log-log plot at high ionic strength.

Increasing ionic strength reduces the electrostatic attraction between the surfactant and the charged surface, thus delaying the onset of the monolayer formation. This is depicted in Figure 1.4a by the bottom arrow. The hydrophobic attractive force is a function of the chain length of the surfactant and the ionic strength of the solution. Hydrophobic chain-chain interactions are favoured at high ionic strength, and these result in a shifting of the second step to lower surfactant concentrations. Thus, as the ionic strength increases, the two transitions move toward each other. Ultimately, the two transitions coalesce, so that there is only a single step as shown in Figure 1.5. The effect of increasing ionic strength on the

shape of an adsorption isotherm can be followed in a study written by Koopal, Lee & Bohmer (1995). The plateau measured at high ionic strength is usually higher than the second plateau obtained from a low ionic strength solution. At high ionic strength, the ions of the electrolyte screen the surface charges, decreasing the repulsion forces between the surfactant head groups, thus allowing close-packing of surfactants on the surface.

1.4.7 Adsorption of surfactants at the solid-liquid interface; Adsorption from mixtures

Adsorption of surfactants from a mixture of surfactants or from a mixture of a surfactant and other, non-surfactant type organics has been intensively studied (Desai and Dixit 1996; Favoriti, Mannebach & Treiner 1996). Surfactants can increase the adsorption of polymers (Neivandt *et al.* 1997) or can promote adsorption of hydrophobic solutes that do not adsorb at the interface between mineral and water in the absence of surfactants. This process is referred as surface solubilization or adsolubilization. This phenomenon brings up environmental issues with respect to clay minerals and soil chemistry (Esumi, Matoba & Yamanaka 1998; Klumpp, Heitmann & Schwuger 1993).

The solubilization of different compounds shows different adsorption isotherm shapes. With increasing surfactant concentrations, the solubilization isotherm of pesticides on laponite shows a competitive adsorption with a cationic surfactant (Esumi, Matoba & Yamanaka 1998). A continuous increase of phenoxyalcohols, styrene and isoprene on silica surface has been measured in the presence of cationic surfactants (Monticone and Treiner 1994a, Kitiyanan *et al.* 1996). For chemicals, such as sodium salicylate, phenol, naphthalene derivatives, the solubilization isotherms measured on surfaces of silica, alumina or quartz show a curve going through a maximum (Schieder *et al.* 1994; Nayyar, Sabatini & Harwell 1994; Favoriti, Mannebach & Treiner 1996; Favoriti, Monticone & Treiner 1996; Monticone, Mannebach & Treiner 1994; Monticone and Treiner, 1994b).

1.4.8 Adsorption of surfactants at the solid-liquid interface; Application of cationic surfactants

Surfactants are among the most versatile products of the chemical industry. They have been used in products as diverse as motor oils, detergents, pharmaceuticals and mineral flotation additives. More recently, surfactants have found application in technologies such as electronic printing, biotechnology, microelectronics, corrosion techniques or viral research. They are ideally suited for use as surface modifiers, fabric softeners or weed control additives. The cosmetic industry applies them in different conditioner products.

This study is focused on the application of quaternary amines as liquor oxalate stabilizers in the Bayer process

1.5 Research objectives

The overall aim of this work has been to investigate how quaternary amine salts affect the precipitation of sodium oxalate, and to understand the mechanisms, at a molecular level, by which specific additive molecules stabilize a high level of supersaturation of sodium oxalate in Bayer liquors in the presence of sodium oxalate seed. This overall aim was achieved by the following measurements:

- Undertake literature search in order to gain an understanding how quaternary amines generally adsorb onto surfaces.
- Obtain a range of quaternary amines with acceptable purity.
- Carry out screening tests to classify quaternary amines in plant and in synthetic liquor.
- Identify optimum conditions, seed charge, adsorption time and oxalate supersaturation for the screening test.
- Measure the effect of other organic components in the liquor on the stabilization capacity of quaternary amines.
- Measure adsorption isotherms for selected compounds. The effect of conditions will be investigated.
- Observe the nature of adsorption of additive molecules using surface investigation techniques.

It was intended that (partial) answers to the following questions be found:

* How does a sodium oxalate seed stabilizer work?
* How do stabilizer molecules adsorb onto sodium oxalate crystal faces?
* What makes a good stabilizer molecule, and how do we make a better one?
* Do the other organics present in plant liquors affect the action of stabilizers, and if so, how?

Chapter 2

The Effect of Quaternary Amines on the Crystal Growth of Sodium Oxalate

2.1 Introduction

Quaternary Amines (QAs) were found to be effective oxalate stabilizers in plant process liquors; they increased the stability of liquor (the highest oxalate concentration, that the liquor can tolerate without co-precipitation for 24 hours, Farquharson *et al.* 1995b).

The effect of QAs on liquor stability was determined with the MOST test (Miniaturised Oxalate Stability Test) (Farquharson *et al.* 1995b; Farquharson *et al.* 1996). This test simulated the plant conditions, ie alumina trihydrate and sodium oxalate crystals were present. However, the concentration of solid oxalate in this system was very low. It has not been clarified whether this test measures the nucleation or crystal growth of sodium oxalate, or both simultaneously occur during the test. Moreover, the QAs tested with MOST tests were commercial products, consisting of a mixture of QAs.

The principal aim of this work was to determine the effect of QAs on oxalate crystallization. For this, it was necessary to simplify the MOST test conditions. Accordingly, QAs were tested in the MOSPIT test (Miniaturised Oxalate Seed Poison Impact Test), which clearly measured the effect of QAs on the crystal growth of sodium oxalate (McKinnon *et al.* 1998). It was decided to test the active components of the products used in MOST tests (Table I on page 45). If the active component of the previously tested product was not available as a pure chemical with more than 95% purity, a chemically similar compound with acceptable purity was chosen.

2.2 Experimental

2.2.1 Materials

Chemicals: Octadecyltrimethylammonium bromide 98% (C18QA), hexadecyltrimethylammonium bromide (C16QA), tetradecyltrimethylammonium bromide (C14QA), dodecyltrimethylammonium bromide (C12QA), decyltrimethyl-ammonium bromide (C10QA), hexadecylpyridinium chloride (C16PyrQA), hexadecylbenzyldimethylammonium bromide (C16BenQA), hexadecylethyl-dimethylammonium bromide (C16EtQA) and dihexadecyldimethylammonium bromide (DiC16QA) were obtained from Fluka Chemical Company. Nalco Chemical Company supplied N138 and N138#, the active component of N138, reagents. Alcoa supplied the C31 (Al_2O_3*$3H_2O$). All other chemicals used were of analytical grade.

Seed: Clean acicular sodium oxalate was provided by Alcoa. The surface area was determined with the BET method, and was found to be 1 m^2/g. The average crystal size was 30 μm with an aspect ratio of 10:1.

2.2.2 Oxalate analysis

Oxalate concentrations of liquors were determined using the method developed by Grocott (Grocott, 1988). The oxalate concentrations were measured via the dimethyl esters of oxalic acid using capillary gas chromatography.

2.2.3 Conditions

Synthetic liquor used contained the main inorganic components of plant liquor at concentrations as follows: alumina trihydrate (C31: 104 g/L), sodium hydroxide (180 g/L), sodium carbonate (43 g/L), sodium chloride (40 g/L), sodium sulphate (10 g/L), silicic acid (SiO_2: 0.5 g/L), sodium phosphate (P_2O_5: 0.3 g/L), sodium formate (5 g/L), sodium acetate (20 g/L), sodium malonate (5 g/L) and sodium succinate (15 g/L). The characteristics of these liquors given in terms used at Alcoa's refineries are total alkaline= 280 g/L, total caustic/total alkaline = 0.84, Al_2O_3/total caustic = 0.28 and Al_2O_3/total caustic = 0.3 (low, to ensure the liquors were stable with respect to gibbsite precipitation). The liquors were equilibrated

with sodium oxalate at 60 °C for 5 hours prior to use. The concentration of oxalate in these liquors was 0.70 ±0.03 g/L.

Plant process liquor: Portions of plant process liquor were taken from the plant at Kwinana refinery. Samples came from liquor (Kelly filtrate) containing high concentration of plant organics. The concentration of oxalate in plant liquors was around 2.5 g/L.

Temperature: all of the experiments were carried out at 60 °C.

2.2.4 Procedures

The MOSPIT test developed by Alcoa was used. The standard method involved equilibrating acicular oxalate seed crystals in synthetic liquor, containing the quaternary amines or other test organics, or in plant process liquor. Samples in test tubes were conditioned in a rotating water bath. Once equilibrated, the solutions were supersaturated with sodium oxalate by increasing the dissolved sodium oxalate concentration. The start oxalate concentration was measured. Then crystallization proceeded. After one hour crystallization time, the solutions were filtered, and the soluble oxalate concentrations of liquors were measured. The difference between the oxalate concentrations at the start and end of crystallization gave the yield. The stronger the crystal growth inhibition, the lower the yield. In the absence of seed, no crystallization occurred. The precision of the test has been determined to be ±0.1 g/L. Figure 2.1 shows the concentration of sodium oxalate measured for the standard MOSPIT conditions in synthetic liquor with time.

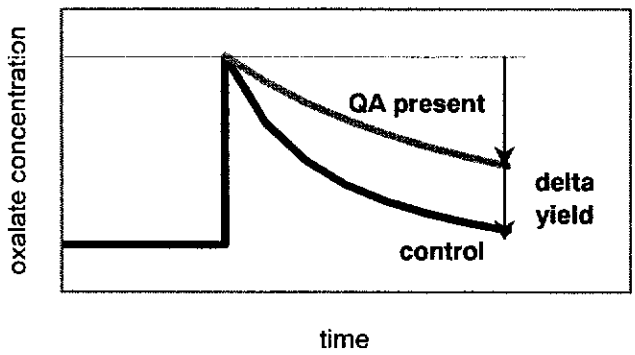

Figure 2.1: Schematic diagram of oxalate concentration during MOSPIT test

2.3 Results and Discussions

2.3.1 Containers

It was found that the QAs tested in different containers gave different MOSPIT results. Thus, the question arose at the beginning of this work as to which would be the best type of vessel that should be used during the work.

Dealing with surfactants, another important question arose concerning how much surfactant adsorbs onto the surface of the vessel. This would decrease the actual concentration of surfactant affecting the oxalate crystallization, and should be taken into account if it is significant. This effect was measured, and the results are reported in Chapter 3.

MOSPIT tests were carried out in culture tubes (made of glass), in FEP bottles (made of Teflon) and in centrifuge tubes (made of polypropylene). It should be noted, however, that the FEP bottles had a much higher volume, 250 mL, than the test tubes. Therefore, the MOSPIT test was carried out with a much higher volume of liquor in these bottles; and the test conditions were adjusted proportionately. The effects of N138 and C18QA on oxalate yield were determined in synthetic and in plant liquors (Figure 2.2).

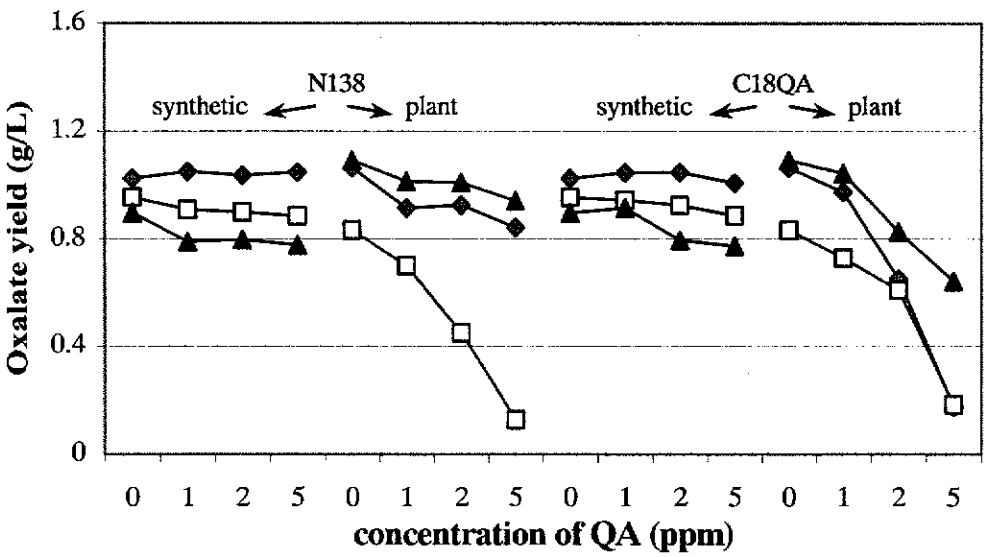

Figure 2.2: MOSPIT results of N138 and C18QA measured in different vessels (diamond: in glass, square: in polypropylene, triangle: in teflon) in plant (16/10/96 Kwinana) and in synthetic liquors

Figure 2.3 presents the repeated experiment for N138 and C18QA, and the MOSPIT results of C12QA and C16BenQA measured in synthetic liquor in glass and polypropylene containers.

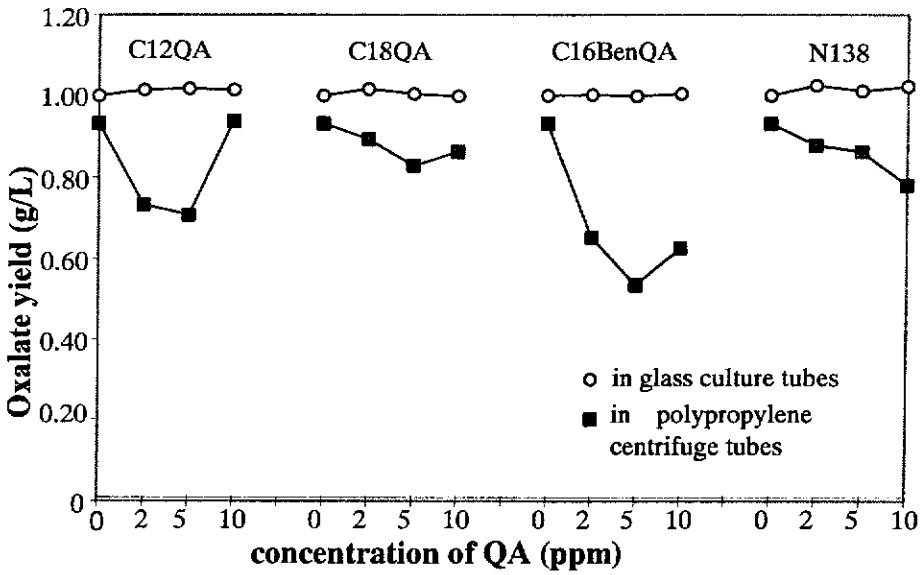

Figure 2.3: MOSPIT results of C12QA, C18QA, C16BenQA and N138 in synthetic liquor measured in glass and polypropylene containers

It was found that QAs inhibited oxalate crystal growth in synthetic liquors measured in polypropylene tubes, and they did not in glass containers. Results measured in Teflon vessels were very similar to those found in glass culture tubes. Small differences may have been due to the different volumes of the containers, and also, the different hydrodynamics.

Further investigations indicated that the effect of QAs measured in polypropylene was proportional to the amount of plastic in contact with the liquor. Figure 2.4 shows the MOSPIT results carried out in culture tubes (glass), centrifuge tubes (polypropylene) and culture tubes with extra pieces of centrifuge tube in them.

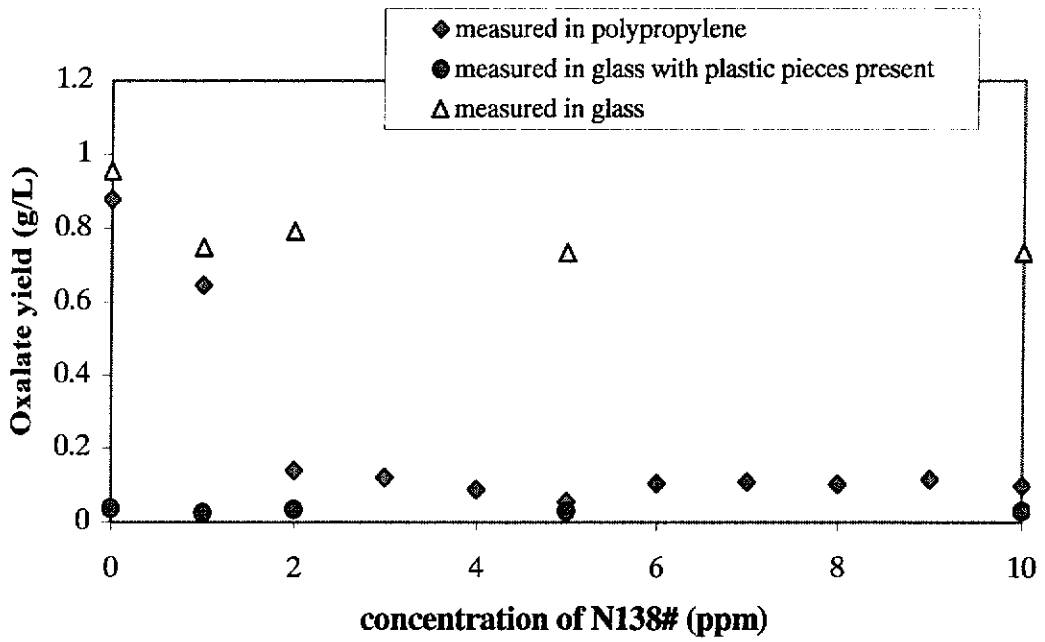

Figure 2.4: MOSPIT results of N138# in culture tubes (glass), in centrifuge tubes (polypropylene) and in culture tubes with centrifuge tube pieces in them in plant liquor (16/10/96 Kwinana)

MOSPIT results from tubes with plastic pieces show a very inhibited crystal growth at every dose of N138# including 0 ppm. The anomalous results measured in plastic centrifuge tubes are probably due to the plasticizer leached out under liquor conditions. Sodium stearate is a generally used additive in the polypropylene production.

As glass culture tubes seemed to be more suitable for the work, all of the subsequent experiments were carried out in glass vessels.

2.3.2 Classification of QAs in plant liquor

QAs have been classified as strong, medium or weak stabilizers with the MOST test. It was decided to carry out a similar classification with the MOSPIT test, and classify the QAs as strong, medium or weak crystal growth inhibitors in plant liquor. Then, results from the MOSPIT tests were compared with those of the MOST tests. If the active component of the commercial product tested in the MOST test was not available as a pure chemical with more than 95% purity, a chemically similar compound with acceptable purity was chosen.

The oxalate yields in MOSPIT tests were determined as a function of the concentration of QAs in plant liquor. Then, the classification was carried out in an arbitrary way: when the MOSPIT yield of an inhibitor was between 0-33% of the control yield at 5 ppm concentration of quaternary amine, it was considered to be a strong inhibitor. For a medium inhibitor, the yield was between 33-66% of the control yield, and for a weak inhibitor, the yield was above 66% of the control yield at a concentration of 5 ppm QA. Classification was carried out at an inhibitor concentration of 5 ppm to compare the results with each other, since the difference in yields was the greatest at this dose. It is also compatible with the MOST results (Farquharson *et al.* 1996). Figure 2.5 shows the test results at different concentrations of C10QA, C12QA, C18QA and N138# compounds, as representatives of the examined QAs. Results of the remaining QAs tested are shown in Appendix 2 (Figure 2 .12 and 2.13). TABLE I contains the classification of QAs in terms of both MOSPIT and MOST results.

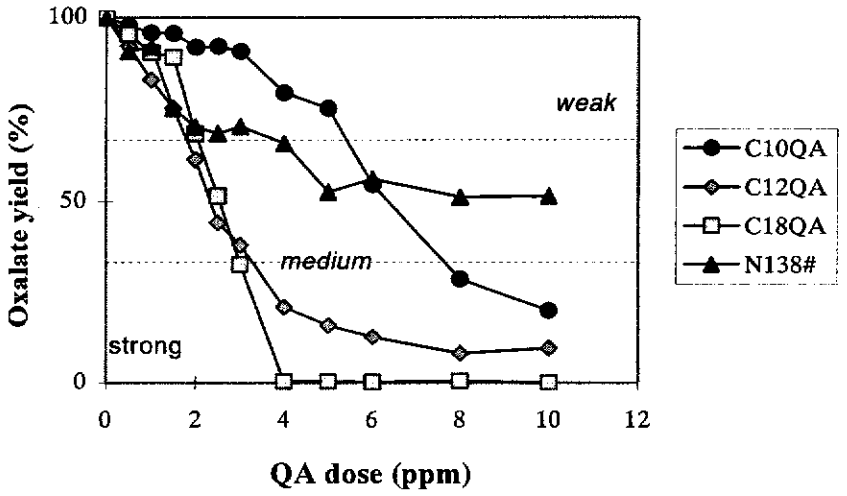

Figure 2.5: MOSPIT results of C10QA, C12QA, C18QA and N138# in plant liquor.

TABLE I: Classification of QAs in plant liquor

inhibitor/stabilizer	MOSPIT	MOST
C10QA	WEAK	STRONG
C12QA	STRONG	STRONG
C14QA	STRONG	-
C16QA	STRONG	STRONG
C18QA C16-20 mixture	STRONG	 STRONG
N138 (5 ppm)	-	STRONG
N138 (15 ppm)	WEAK	-
N138# (5 ppm active)	MEDIUM	-
C16EtQA C17EtQA	STRONG	 STRONG
C16PyrQA C12PyrQA	MEDIUM	 MEDIUM
C16BenQA C12BenQA	WEAK	 MEDIUM
DiC16QA DiC10QA	WEAK	 WEAK

- : chemical was not tested

2.3.3 Comparison of the performance of QAs in MOSPIT and in MOST tests

It has generally been assumed that QA molecules stabilize oxalate in solution by adsorbing onto oxalate nuclei, thus preventing their growth. If this is the way that QAs stabilize the oxalate, the order of the strength of stabilizers and that of inhibitors must be the same more or less. The order of the strength of QAs in both tests is generally the same. A strong stabilizer is almost always a strong crystal growth inhibitor; there were only two exceptions: the C10QA and N138. However, it should be noted that the MOST tests were carried out in polypropylene tubes. MOST tests of some of the QAs were repeated in glass culture tubes. These results indicated that the classification of QA stabilizers may have been affected as a result of the effects of plasticizers leaching from the polypropylene. N138 was not as effective in glass

vessels as measured in polypropylene tubes (McKinnon *et al.* 1998). MOSPIT tests were carried out in glass culture tubes.

Based on these results, it is very possible that the two tests, MOSPIT and MOST, measure the same phenomenon, ie the inhibition of the crystal growth of sodium oxalate. Futhermore, these results seem to confirm the original concept that the QA stabilizers in plant liquor act via the inhibition of crystal growth of sodium oxalate.

2.3.4 Effect of QAs in synthetic liquor under different conditions

To clarify the action of QAs in plant liquor and to characterize their effect, it was attempted to reproduce the same behaviour of QAs, as found in plant liquor, in synthetic liquor with the main characteristics of the plant liquor (pH, ionic strength). Two exceptions are the absence of plant organics and trace elements. It was found that no QA had any effect on oxalate yield in synthetic liquor under the standard MOSPIT conditions (Figure 2.6).

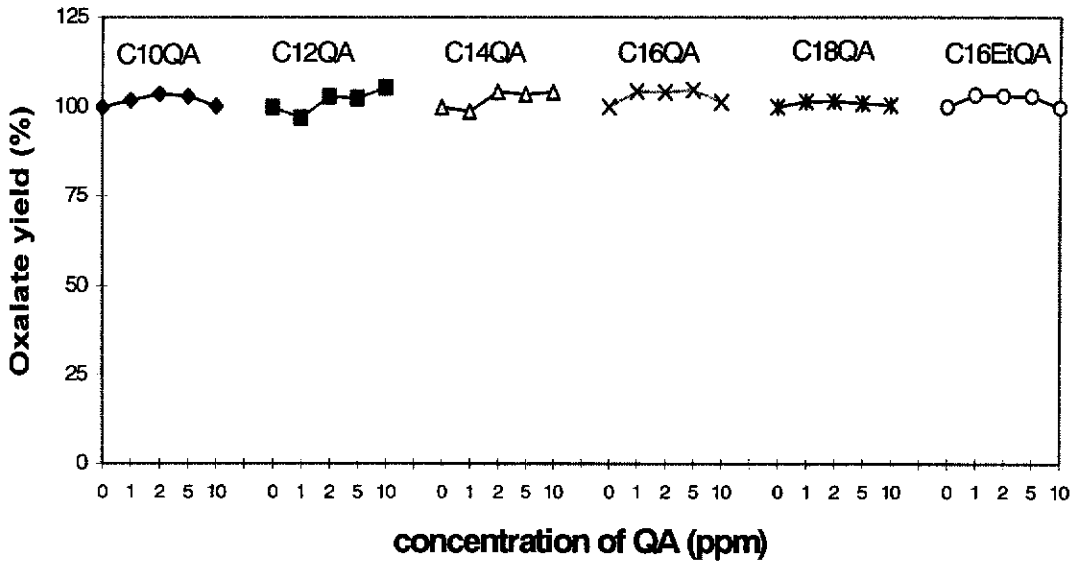

Figure 2.6: MOSPIT results of C10QA, C12QA, C14QA, C16QA, C18QA and C16EtQA in synthetic liquor

To test the effect of a broad range of conditions on the activity of QAs, the following parameters in the experiments were varied:

Varying supersaturation and seed charge

The effects of varying the start oxalate concentration (raised by 0.9-1.5 g/L) and seed charge (0.5-1.0 g/L) on the oxalate yield were investigated in the presence of N138# in synthetic liquor (Figure 2.7). It was thought that a low supersaturation and seed charge might make a small inhibition effect easier to see.

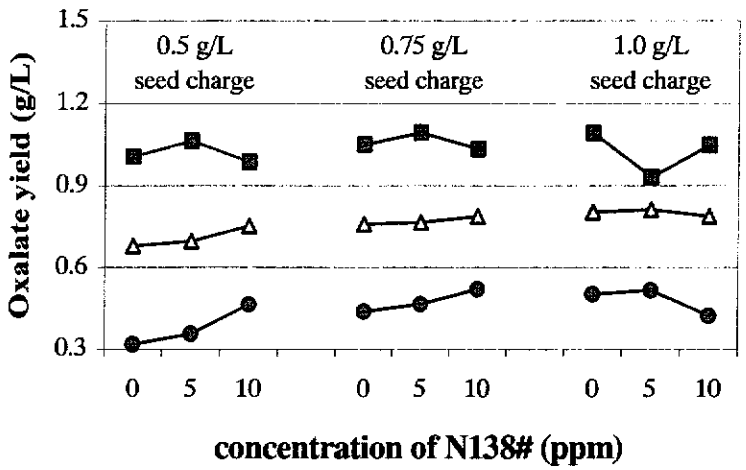

Figure 2.7: MOSPIT results of N138# at different oxalate boost (square: 1.5 g/L, triangle: 1.2 g/L and circle: 0.9 g/L) and seed charge in synthetic liquor

Decreased ionic strength

The effects of C10QA, C12QA, C14QA, C16QA, C18QA and C16EtQA on oxalate yield were determined by MOSPIT tests in synthetic liquor diluted to 75% of their original ionic strength. This dilution was intended to result in higher CMCs of the examined QAs, and so, higher concentrations of free QA molecules in solution (section 1.4.3).

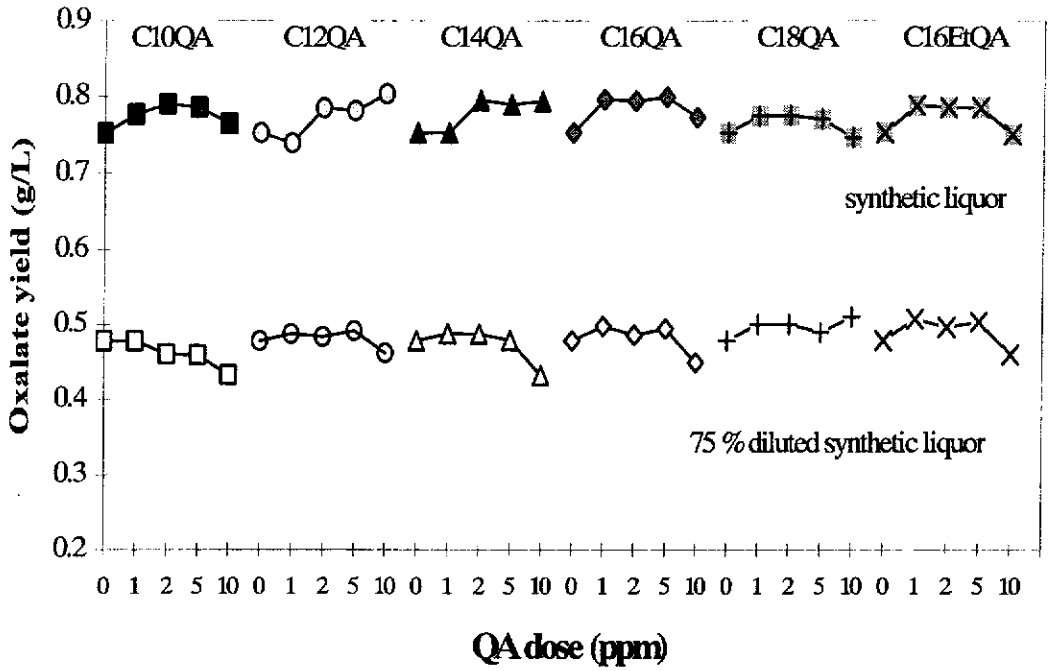

Figure 2.8: MOSPIT results of C10QA, C12QA, C14QA, C16QA, C18QA and C16EtQA in synthetic liquor and in diluted synthetic liquor

Changed liquor composition

MOSPIT tests were carried out in the presence of C12QA, C18QA and C16BenQA in synthetic liquors of various compositions (Figure 2.9). Synthetic liquor I contained sodium malonate and sodium succinate. Synthetic liquor II was prepared without these chemicals. In the latter synthetic liquor, the QAs had a much higher surface activity. Synthetic liquor III was diluted from liquor I (ratio: 3:4).

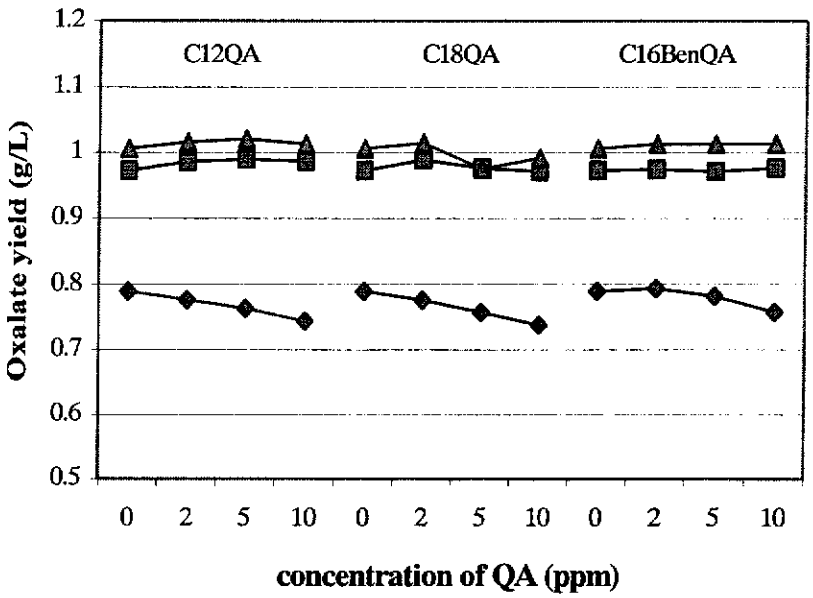

Figure 2.9: MOSPIT results of C12QA, C18QA and C16BenQA in different synthetic liquors (square: liquor I, triangle: liquor II, diamond: liquor III).

Batch crystallization runs

Crystallization runs in a steel crystallizer of 5L capacity were carried out in the presence of 10 ppm N138 or C16EtQA. Figure 2.10 shows that no impact on the desupersaturation rate was found in the presence of 10 ppm C16EtQA. Similar results were measured in the presence of 10 ppm N138 (Appendix 2.14).

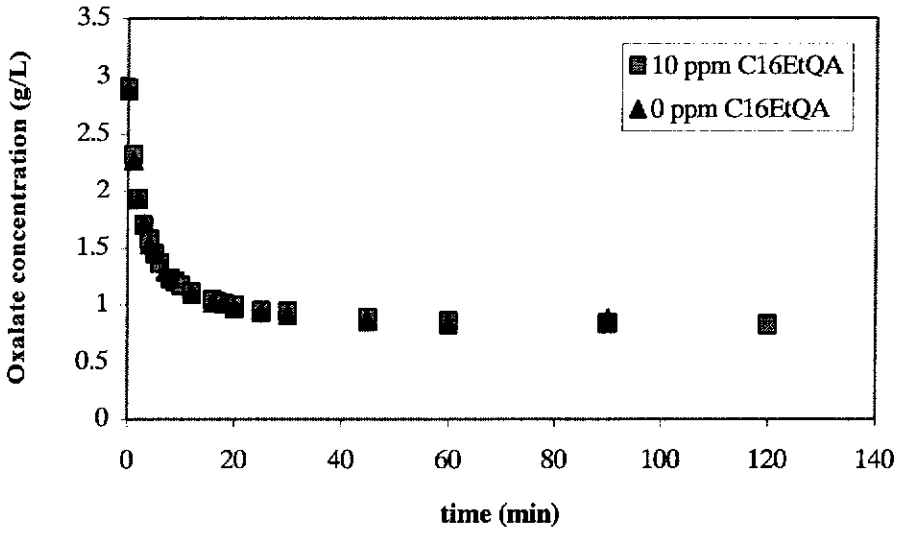

Figure 2.10: The effect of 10 ppm C16EtQA on the desupersaturation rate of sodium oxalate in synthetic liquor.

Under all of the conditions described above, none of the examined QAs had any effect on the oxalate yield in synthetic liquor. Thus, QAs do not inhibit crystal growth of sodium oxalate in synthetic liquors under the applied conditions.

2.3.5 Effect of QAs in blend liquor

It was found that QAs inhibited oxalate crystal growth in plant liquors very well, and they did not do so in synthetic liquors. Then, the effect of QAs was measured in blends of synthetic and plant liquors.

Blend liquors were made up by simply mixing plant liquor (Kelly filtrate, 10/1/97) and synthetic liquor saturated with sodium oxalate. The effect of C12QA, C18QA and C16BenQA on the oxalate yield was determined in various compositions of blends of plant and synthetic liquors. Figure 2.11 shows the results of C12QA. Appendix 2 (Figure 2.15 and 2.16) contains the results of C18QA and C16BenQA.

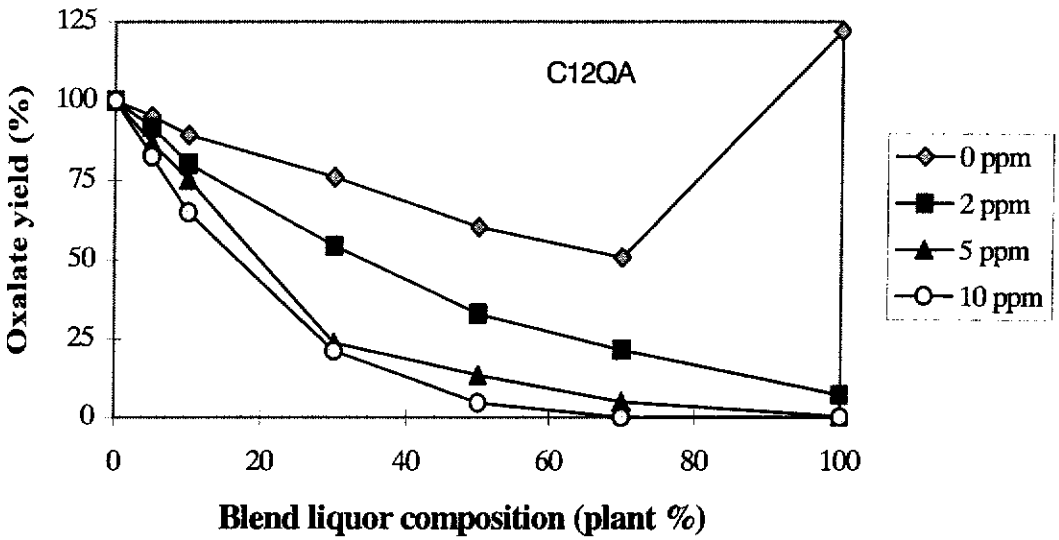

Figure 2.11: MOSPIT results of C12QA in blend liquors

The yield measured from synthetic liquor was considered 100%. Control yields (0 ppm QA) vary significantly with the composition of blend liquors. The curve goes through a minimum, and this behaviour is probably due to a combination of two opposing effects. The supersaturation varies with the composition of the blend (it was measured that the equilibrium saturation level of oxalate in plant and synthetic liquors is almost the same, but the concentration of dissolved oxalate in plant liquor is significantly higher). In isolation, this difference would tend to make the precipitation rate faster, and the yield would be bigger with increasing percentage of the plant component. However, in addition, there is the effect of the poisoning the crystal growth of sodium oxalate by plant organics, OSPs (Oxalate Seed Poisons), in the plant liquor component. Increasing concentration of poisons from plant liquor with increasing blend composition would result in decreasing precipitation rates and decreasing yields. The measured yields at low plant composition blends indicate the strong inhibition of precipitation by increasing concentration of poisons from the plant component, while yields at high blend compositions (> ca 70 plant %) show the effect of higher supersaturation overcoming the inhibition effect of the poisons. The addition of QAs introduces an additional effect. QAs inhibit crystal growth in blend liquors but not in synthetic liquors. The non-linearity of the decrease in oxalate yield induced by the QAs indicates that a small amount of plant liquor (10%) is enough to cause a significant decrease in yield.

2.4 Conclusions and Recommendations

2.4.1 Conclusions

MOSPIT results measured in different containers revealed that the test gives an anomalous response when carried out in polypropylene test tubes. At the beginning of the work, it was important to test different containers for suitability. Glass culture tubes were found to be suitable for further test work.

QAs were classified as strong, medium or weak crystal growth inhibitors in plant liquor using the MOSPIT test. All of the QAs tested had an effect on the oxalate yield. Results showed that the order of the strength of QAs followed the same trend in both MOST and MOSPIT tests.

As the characteristics of a plant liquor change from day to day in a plant, depending on the operation conditions and the bauxite quality, it was decided to use synthetic liquor of constant composition in order to clarify the action of QAs in liquor and to get consistent data. However, QAs do not inhibit oxalate crystal growth in synthetic liquor. This must be due to one of the two differences between synthetic and plant liquors, ie the absence of plant organics or trace elements. The influence of plant organics was more likely.

One way to increase the organic content of the liquor was to make up blends of synthetic and plant liquors. QAs were tested in these blends and were found to be effective inhibitors. It was measured that a small amount of plant organics was sufficient to induce the inhibitory effect of QAs. These results confirmed that plant organics play an important role in the action of QAs in plant liquor.

2.4.2 Recommendations

Results from different containers indicated that one needs to be extremely careful when working with solutions such as the Bayer liquor. The extremely high pH of the liquor attacked the plastic, causing false test results. As a result of this observation, all of the plastic and rubber materials being in contact with liquor, especially when the liquor was hot, were tested prior to use. During this work, there was concern for the organic contamination only, therefore, glass and steel vessels were applied whenever possible.

It is recommended that the synthetic liquor should be treated with activated carbon prior to commencing any tests assessing organic additives. The treatment will remove other organic impurities coming from chemicals used for preparing the synthetic liquor. Due to the huge amount of material, ca 500 g/L, from which the liquor is made, the level of impurities can be high.

Many QAs were found to be more effective in plant liquor than the N138 that has been currently used in the plant. From the chemical point of view, C18QA, C16QA, C14QA, C12QA or C16EtQA should be more favoured for use as an additive in the process liquor to stabilize oxalate. Of course, a plant might have economic reasons to choose a stabilizer with moderate stabilizing strength.

Appendix 2

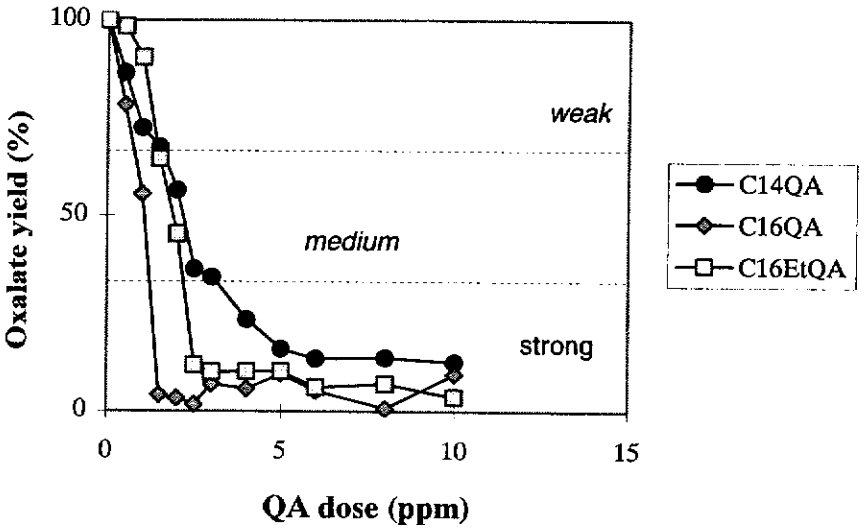

Figure 2.12: MOSPIT results of C14QA, C16QA and C16EtQA in plant liquor (16/10/96)

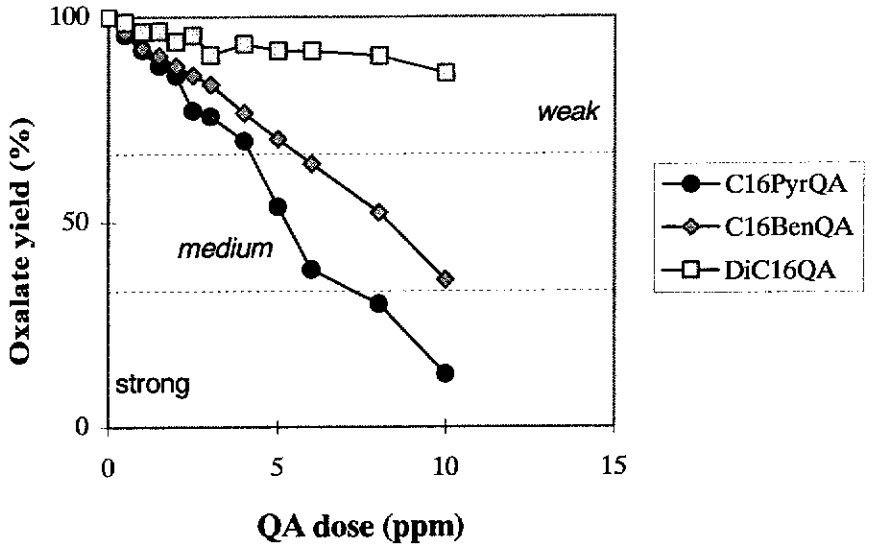

Figure 2.13: MOSPIT results of C16PyrQA, C16BenQA and DiC16QA in plant liquor (16/10/96)

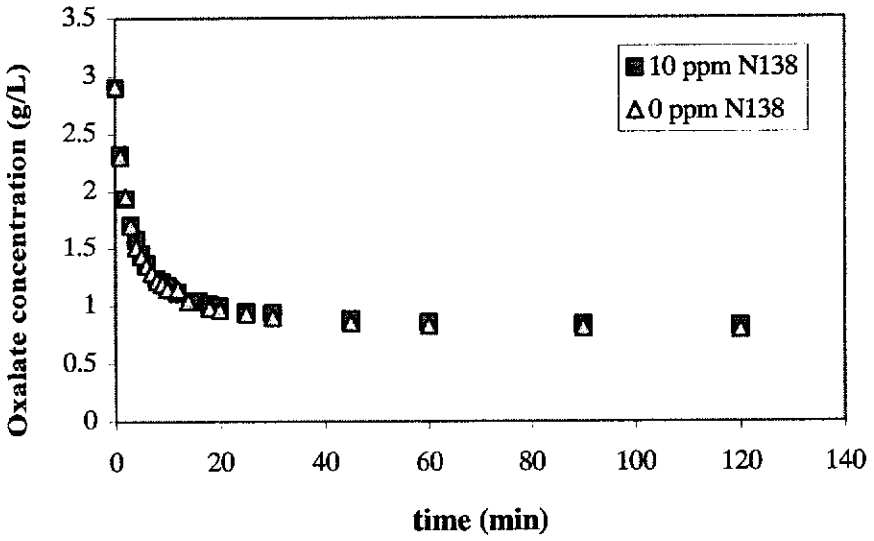

Figure 2.14: The effect of 10 ppm N138 on the desupersaturation rate of sodium oxalate in synthetic liquor.

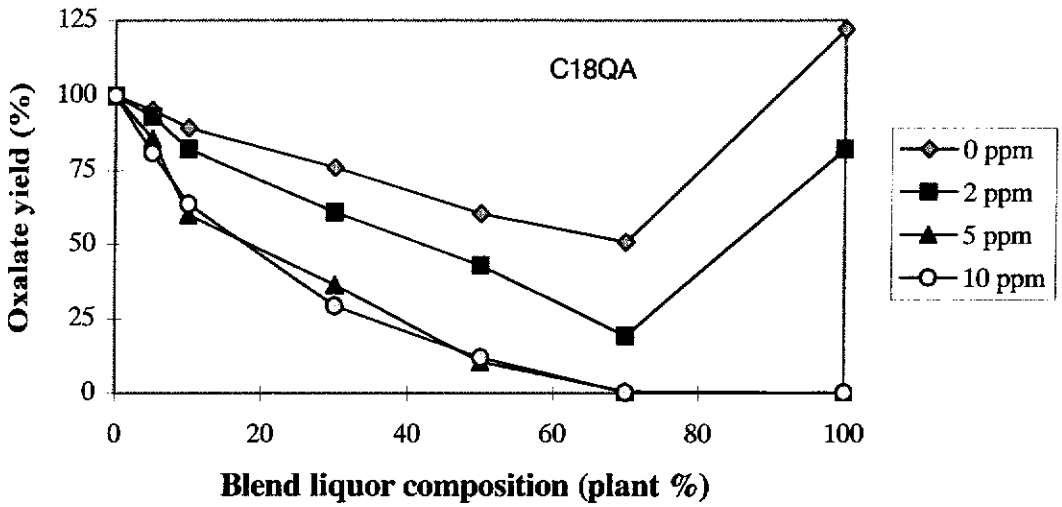

Figure 2.15: MOSPIT results of C18QA in blend liquors

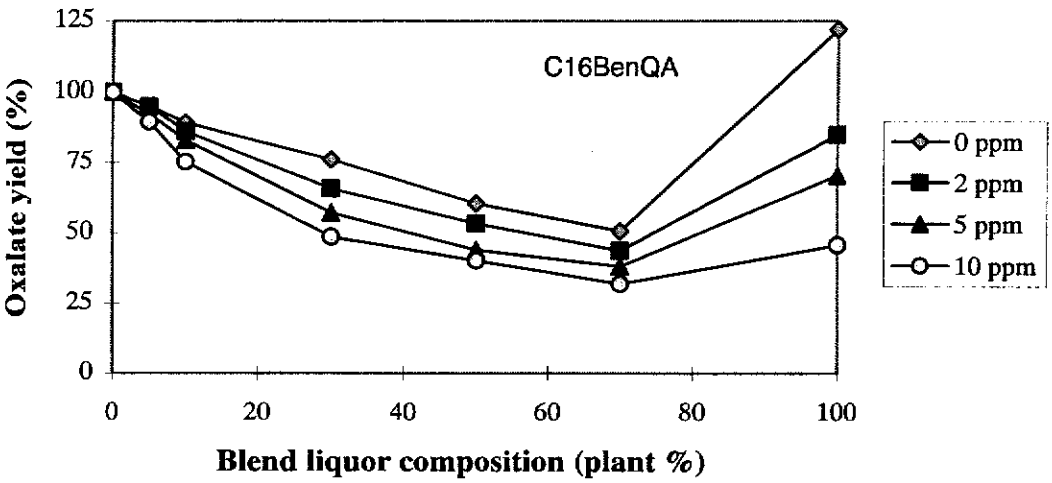

Figure 2.16: MOSPIT results of C16BenQA in blend liquors

Chapter 3

The Effect of Quaternary Amines on the Crystal Growth of Sodium Oxalate in the Presence of Plant Organics or Model Organics

3.1 Introduction

QAs do not inhibit sodium oxalate crystal growth in synthetic liquor. The reason that QAs inhibit crystal growth in plant liquor and blend liquors must be due to synergy with some of the organic content of the plant liquor. It was decided to examine the effect of QAs on the crystal growth of sodium oxalate in the presence of plant organics and model organics.

Organics trapped in the solid sodium oxalate precipitated in the plant (Oxalate Cake) or dissolved in the plant process liquor were extracted and fractionated. The effect of QAs on oxalate crystallization was repeatedly measured using the MOSPIT test in the presence of these extracts. The impact of extracts in the absence of QAs on oxalate crystal growth was tested as well.

Since only a few components of the extracts have been identified, and their identities are commercially sensitive, a series of chemicals that have some of the characteristics of the extracts or are in some way related were tested. The impact of QAs on sodium oxalate crystal growth was determined in the presence of these chemicals at various concentration ratios.

3.2 Experimental

3.2.1 Materials

Chemicals: Humic acid and sodium humate were obtained from Fluka Chemical Company and Aldrich Scientific Company, respectively. Polyacrylate (M_r=10,000), dextran, polyacrylamide (M_r=1000,000), carboxymethyl cellulose, sodium citrate,

EDTA, sodium dodecyl sulfate and Triton X-100 were purchased from Aldrich Chemical Company. Dodecylbenzene sulfonic acid (97%) was obtained from Acros Organics. Tertiary amines, $C_{12}H_{25}N(CH_3)_2$, $C_{16}H_{33}N(CH_3)_2$ and $C_{18}H_{37}N(CH_3)_2$ were obtained from Kasei Chemical Company. All other chemicals used were of analytical grade.

Extracts: HUMIC cake extract and Low Molecular Weight cake extract (LMW cake extract) were supplied by Alcoa. HUMIC plant liquor extract and LMW plant liquor extract were extracted from plant process liquor using the method described below (Section 3.2.3).

3.2.2 Analysis

LMW-OSP analysis: Low molecular weight organics from plant process liquor were identified and analysed throughout this work using GC-MS by the staff of the Research and Development Department of Alcoa.

Humate analysis: Humic concentrations in synthetic liquor were determined using a Hewlett Packard 8453 UV-VIS spectrophotometer. Absorbances of the humic liquor solutions were determined using a 1 cm or 10 cm pathlength cuvette to record the spectra in the range of 290-560 nm.

3.2.3 Preparation of cake extracts

The method of "Oxalate seed poisons isolation from oxalate belt filter cake" developed by Wai Lim Kong was used to prepare organic extracts. The method involves the dissolution of the solid sodium oxalate cake precipitated in the plant, the acidification of the solution and the extraction with toluene. The organic matter trapped in the precipitated oxalate is then fractionated based on the chemical nature of the components. Three fractions were separated as follows.

a) HUMIC cake extract. During the extraction, the solid phase of precipitated humic acid is accumulated at the toluene/water interface. It is filtered, washed and dissolved in NaOH solution resulting in an aqueous solution with a concentration of 1 g/mL. The concentration of the HUMIC cake extract is expressed as the mass of sodium oxalate from which the humic content is isolated (eg. 1g/L humic solution represents the humic isolated from 1 gram of solid sodium oxalate and dosed into 1L of synthetic liquor).

The total organic carbon (TOC) of the extract was determined and found to be 2.5 mg C/mL.

b) LMW cake extract. Low molecular weight, anionic surfactant type chemicals are accumulated in the organic phase. The majority of the organic solvent is evaporated resulting in a toluene solution with a concentration of 1 g/mL. The concentration of the LMW cake extract is expressed as the mass of sodium oxalate from which the LMW organic content is isolated (eg. 1g/L LMW solution represents the organics isolated from 1 gram of sodium oxalate and dosed into 1L of synthetic liquor).

c) Fulvic acid extract. The organics remaining in the water phase are isolated using ion-exchange columns. This extract was subjected to further separation. The fulvic acid extract was not tested within this work.

3.2.4 Preparation of plant liquor extracts

The above method was found to be suitable for the isolation of organics from plant process liquor (crystallizer feed liquor, Kwinana, 24/4/97) using a 10:1 dilution to prevent salts from depositing during the extraction. Only two fractions were prepared and tested in this work.

a) HUMIC plant liquor extract. The organic content of 20 mL extract is extracted from 1L plant process liquor. The concentration of the HUMIC plant liquor extract dosed into synthetic liquor is expressed as the volume of the extract (eg. 1mL/L HUMIC plant liquor extract solution represents the humic content of 1 mL of extract dosed into 1L of synthetic liquor). The total organic carbon (TOC) of the extract was determined and found to be 2.5 mg C/mL.

b) LMW plant liquor extract. The organic content of 20 mL extract is extracted from 1L plant process liquor. The concentration of the LMW plant liquor extract dosed into synthetic liquor is expressed as the volume of the extract (eg. 1mL/L LMW plant liquor extract solution represents the organic of 1 mL of extract dosed into 1L of synthetic liquor).

3.3 Results and Discussions

3.3.1 Effect of QAs in synthetic liquor dosed with organic extracts from plant liquor and from oxalate cake

The effect of the presence of QAs on oxalate yield in MOSPIT tests was measured in synthetic liquors dosed with organic extracts. The liquor was dosed with the LMW or HUMIC extract from oxalate cake or from plant liquor prior to the addition of QA. The impact of C12QA, C18QA, C16PyrQA and N138# at various concentrations on oxalate yield was measured using the standard MOSPIT conditions (section 2.2.4). Figure 3.1 and 3.2 show the effects of the above QAs on oxalate yield in the presence of plant liquor extracts.

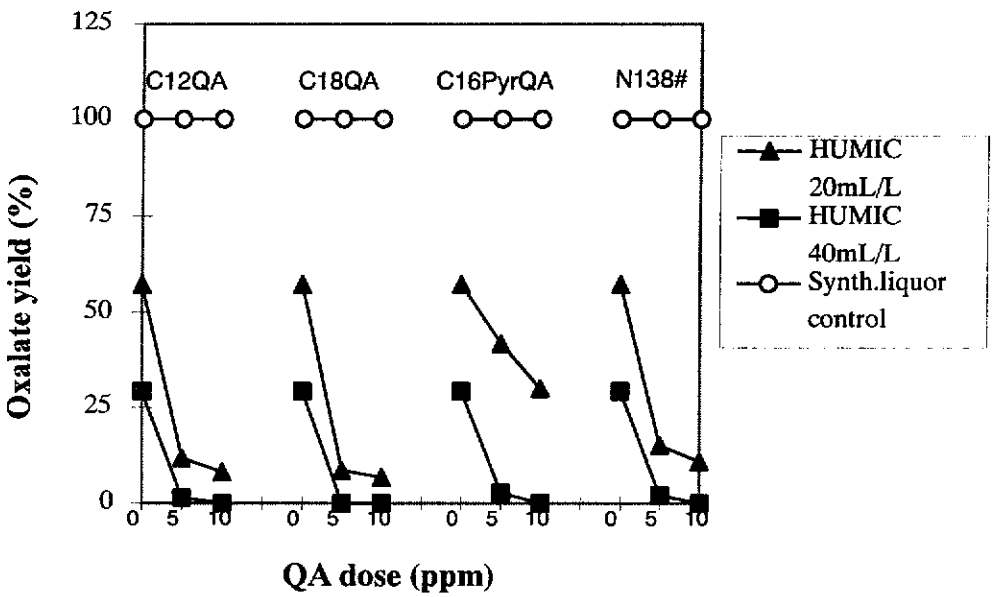

Figure 3.1: MOSPIT results showing the effects of C12QA, C18QA, C16PyrQA and N138# in synthetic liquor dosed with the HUMIC plant liquor extract (20 mL/L is the backdosing level calculated to simulate the concentrations occuring in plant liquors).

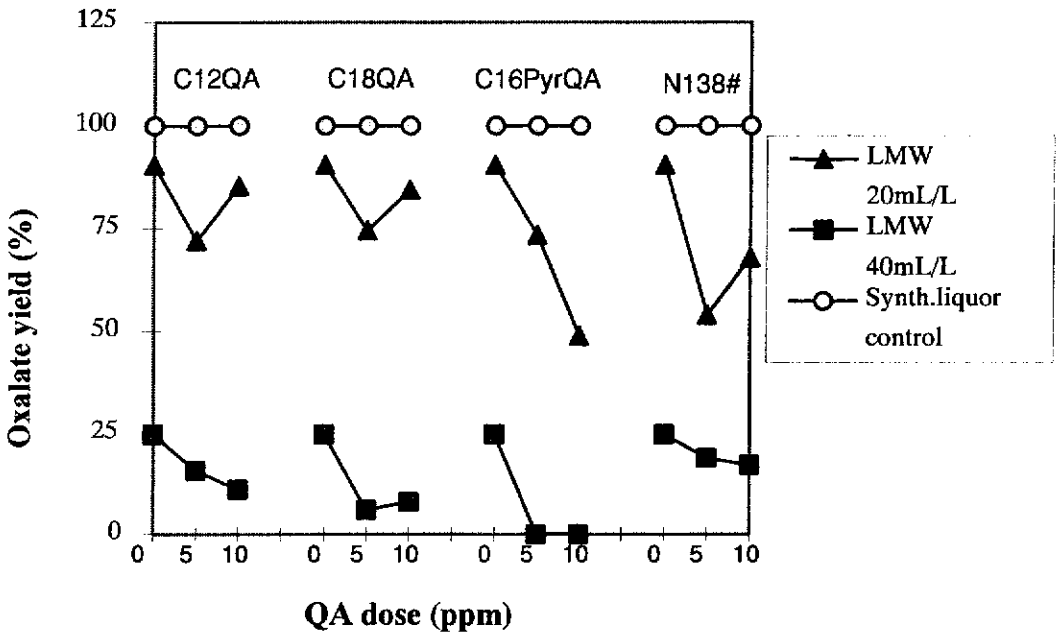

Figure 3.2: MOSPIT results showing the effects of C12QA, C18QA, C16PyrQA and N138# in synthetic liquor dosed with the LMW plant liquor extract (20 mL/L is the backdosing level calculated to simulate the concentrations occuring in plant liquors).

The same QAs had a weaker impact on oxalate yield in the presence of cake extracts (Figures 3.3 and 3.4).

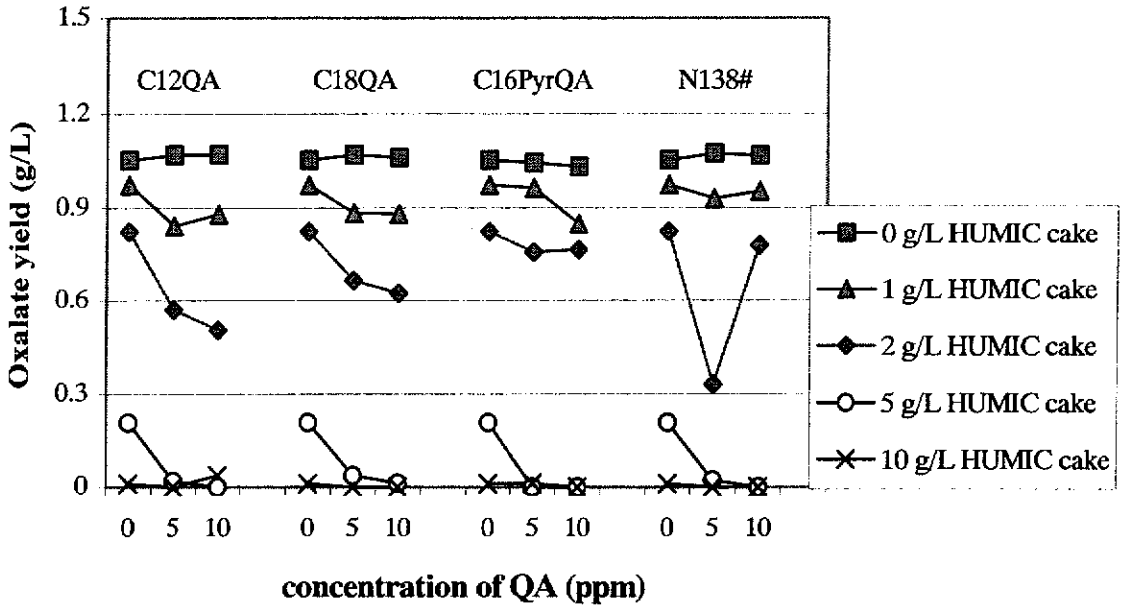

Figure 3.3: MOSPIT results showing the effects of C12QA, C18QA, C16PyrQA and N138# in synthetic liquor dosed with the HUMIC cake extract

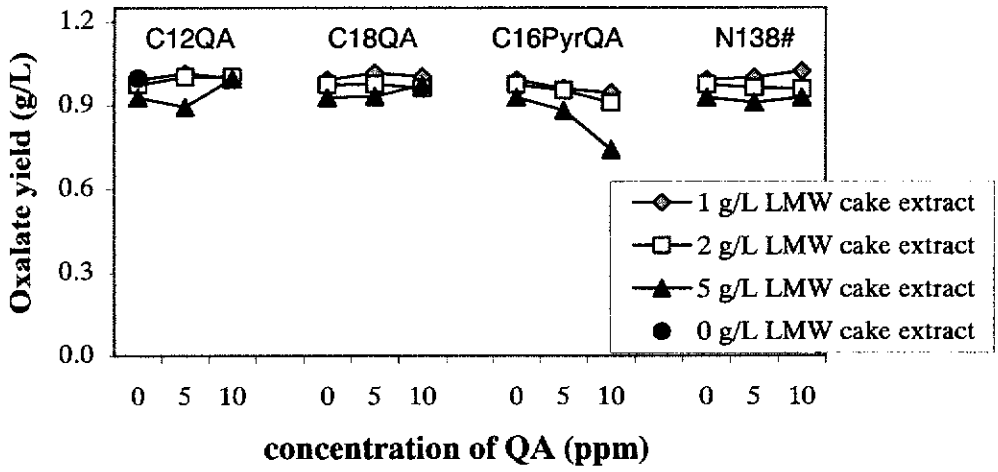

Figure 3.4: MOSPIT results showing the effects of C12QA, C18QA, C16PyrQA and N138# in synthetic liquor dosed with the LMW cake extract

Just the addition of the HUMIC or LMW extracts prepared from plant liquor and the HUMIC extract from oxalate cake on their own (at 0 ppm of QA) had a large impact on the oxalate yield. The decrease in yield was proportional to the concentration of organics present in synthetic liquor. Adding the above QAs into the liquor solution of these extracts further reduced the oxalate yield significantly. In

the presence of humates, the additional effect of QAs was proportional to the QA concentration. However, in the presence of LMW plant liquor extract, the high concentration of QAs often reversed the enhanced inhibitory effect of QAs found at low concentrations. This behaviour was confirmed with other anionic surfactant type compounds of low molecular weight (Section 3.3.6).

It is important to note that the order of the strength of QAs measured in plant liquor (Section 2.3.2) and in synthetic liquor dosed with the HUMIC extracts is the same. A strong crystal growth inhibitor measured in plant liquor is a strong crystal growth inhibitor measured in synthetic liquor dosed with the HUMIC extract. The order of QAs measured in synthetic liquor dosed with the LMW extract varies from that found in plant liquor. Based on these results, it may be inferred that the action of stabilizers in plant liquor is probably due to the presence of humates.

3.3.2 Effect of QAs in synthetic liquor dosed with commercial (Aldrich & Fluka) humic materials

Plant HUMIC extracts inhibited oxalate crystal growth, and an additional effect from the addition of QAs was found. It was decided that other commercial humic materials should be tested for comparison. Liquor solutions of humic materials from Aldrich (HAA) and Fluka (HAF) were made up in 3% NaOH, and tested with MOSPIT test in the presence of 5 ppm of C12QA, C18QA, C16PyrQA or N138#. Figures 3.5 and 3.6 show the results together with those from the following experiments.

The oxalate yield in the presence of commercial humics, HAA and HAF was decreased. HAA and HAF commercial humics were good oxalate poisons. The synergistic effect found between N138# and 30 ppm of HAA or HAF was within the experimental error. The presence of other QAs showed no effect on oxalate crystallization in commercial humic solutions.

3.3.3 Effect of QAs in synthetic liquor dosed with commercial humic materials degraded prior to use

HAA and HAF commercial humics inhibited oxalate crystal growth in MOSPIT tests, however, no synergy was found in the presence of a number of selected QAs. These humics were degraded at high temperature in synthetic liquor and QAs were re-tested in the presence of these degraded humics.

Liquor solutions of the HAA and HAF were made up (250 ppm), and kept in a rotating water bath at 95 °C for 24 hours. The analysis of the humic liquor solutions before and after degradation did not show LMW contaminations at a significant level and the LMW concentrations did not change during the degradation. The chemical effects of the degradation on the commercial humics have not been identified. Figures 3.5 and 3.6 show the MOSPIT results of selected QAs in the presence of 250 ppm or 30 ppm of degraded Aldrich (DegHA) or Fluka (DegHF) humics, or 30 ppm fresh humics for comparison.

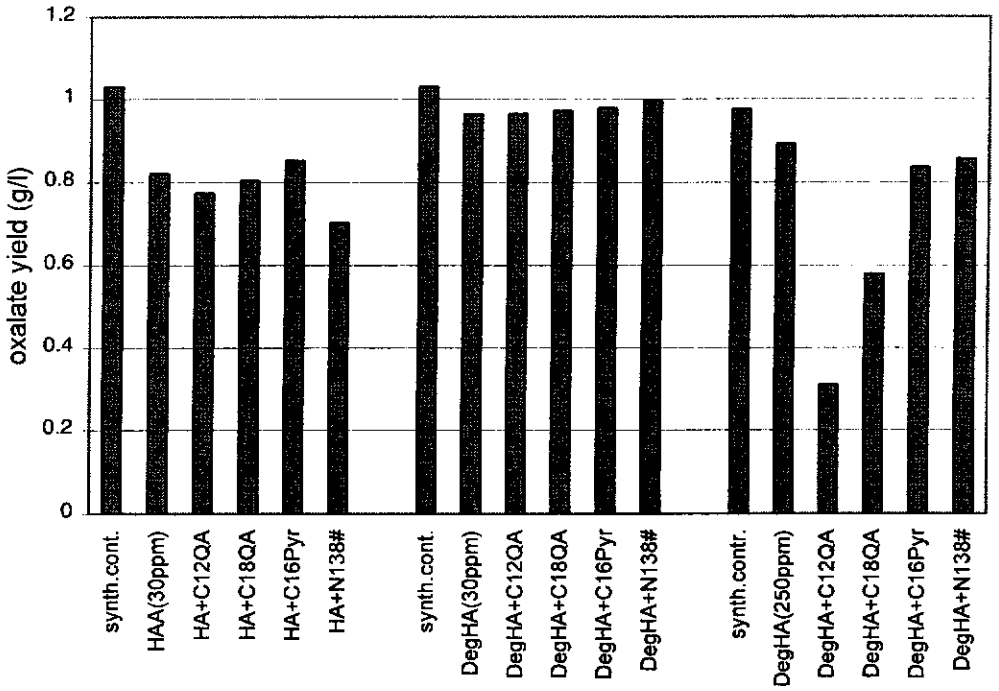

Figure 3.5: MOSPIT results of 5 ppm of C12QA, C18QA, C16PyrQA or N138# in the presence of 30 ppm of fresh Aldrich humics (HAA) and 30 or 250 ppm of degraded Aldrich humics (DegHA) in synthetic liquor

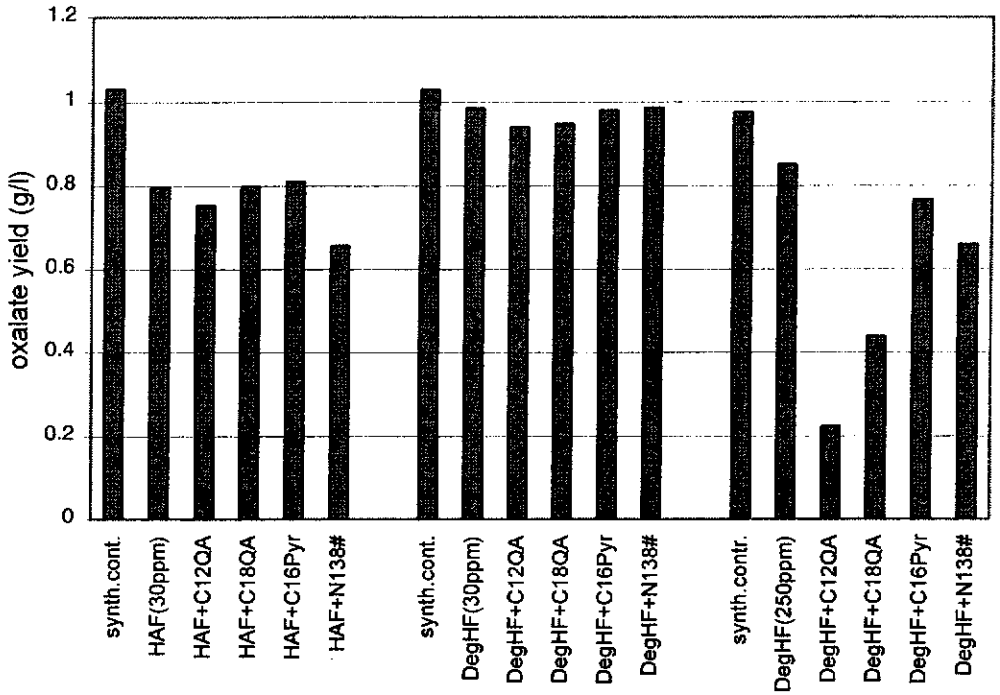

Figure 3.6: MOSPIT results of 5 ppm of C12QA, C18QA, C16PyrQA and N138# in the presence of 30 ppm of fresh Fluka humics (HAF) and 30 or 250 ppm of degraded Fluka humics (DegHF) in synthetic liquor

The degradation of the HAA and HAF commercial humics decreased the poisoning effect. The dosage of 30 ppm of fresh commercial humics, HAA and HAF, was more effective than that of the degraded ones. When the dosage of degraded Aldrich humic, DegHA, is increased to 250 ppm, a synergy was seen with C12QA or C18QA, which was not seen with 30 ppm of fresh humic or 30 ppm of degraded humic. As a result of the degradation of HAF, synergy was found between 250 ppm of DegHF and C12QA, C18QA or N138#.

3.3.4 Effect of QAs in synthetic liquor dosed with polymers

Quaternary amines inhibit oxalate crystal growth in the presence of humates. However, the humic material is not a uniform chemical and its components have not been identified. Accordingly, in order to characterise detailed mechanisms, it is helpful to identify simple model compounds, in the presence of which QAs inhibit oxalate crystal growth, and which exhibit behaviours which are similar to the effect of the humates.

Humates can be characterized by their high molecular weight (500-100,000), anionic functional groups, such as hydroxide, carboxylate, and surfactant nature. A series of chemicals that have one or more of these characteristics was tested using the MOSPIT test. In these experiments, the effect of high molecular weight polymers with uniform functional groups was examined (Figures 3.7 and 3.8).

Liquors were dosed with 10 ppm of polyacrylate, dextran, polyacrylamide or carboxymethylcellulose and 5 ppm of one of the following QAs: C12QA, C18QA, C16PyrQA, or N138#. Model reagents on their own were measured also.

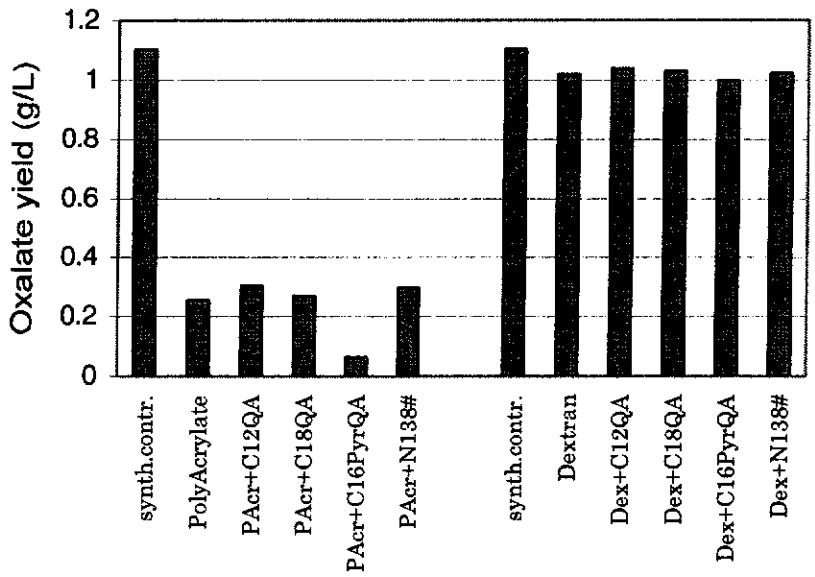

Figure 3.7: MOSPIT results of polyacrylate and dextran (each at 10 ppm) and the effect of the addition of C12QA, C18QA, C16PyrQA or N138#

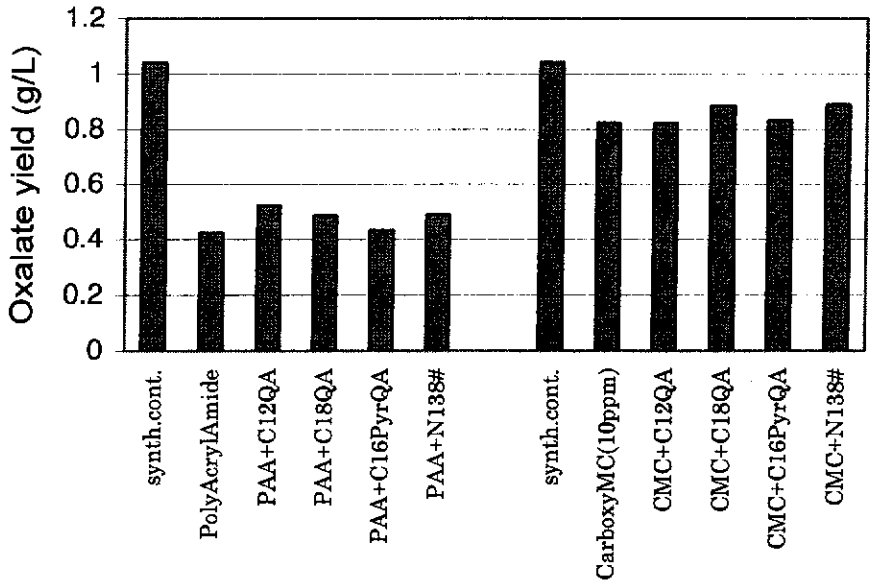

Figure 3.8: MOSPIT results of polyacrylamide and carboxymethylcellulose (each at 10 ppm) and the effect of the addition of C12QA, C18QA, C16PyrQA or N138#

All of the polymers tested decreased the oxalate yield. However, synergy was only found between polyacrylate and C16PyrQA.

3.3.5 Effect of QAs in synthetic liquor dosed with tertiary amines, EDTA and sodium citrate

In these experiments, $C_{12}H_{25}N(CH_3)_2$, $C_{16}H_{33}N(CH_3)_2$ and $C_{18}H_{37}N(CH_3)_2$ tertiary amines, EDTA and sodium citrate were tested. Tertiary amines were measured, because they are produced by the breakdown of QAs at high temperature. EDTA contains four carboxyl functional groups. Citric acid could be considered the simplest model humic as it contains both hydroxyl and carboxyl functional groups.

Liquors were dosed with 10 ppm of either C12QA, C18QA, C16PyrQA or N138#, and their effect was measured in the presence of 30 ppm of either EDTA, $C_{12}H_{25}N(CH_3)_2$, $C_{16}H_{33}N(CH_3)_2$, $C_{18}H_{37}N(CH_3)_2$ tertiary amines or 20 ppm of sodium citrate.

The tested tertiary amines, EDTA and sodium citrate were not oxalate poisons, and no effect was found in the presence of the selected QAs. Results are not shown.

3.3.6 Effect of QAs in synthetic liquor dosed with anionic surfactants

So far, chemicals of high molecular weight or low molecular weight, which had the same functional groups as humates, have been tested. In this experiment, the effect of surfactants, sodium dodecyl sulfate, sodium dodecylbenzenesulfonate anionic and Triton X-100 non-ionic surfactants were investigated.

Synthetic liquors were dosed with 2, 10 or 50 ppm of either sodium dodecyl sulfate, sodium dodecylbenzenesulfonate or Triton X-100, and their effect was measured in the presence of 2, 10 or 25 ppm of either C12QA, C18QA, C16PyrQA or N138#. Figures 3.9-3.17 show the measured oxalate yields at different concentration ratios of surfactants and QAs.

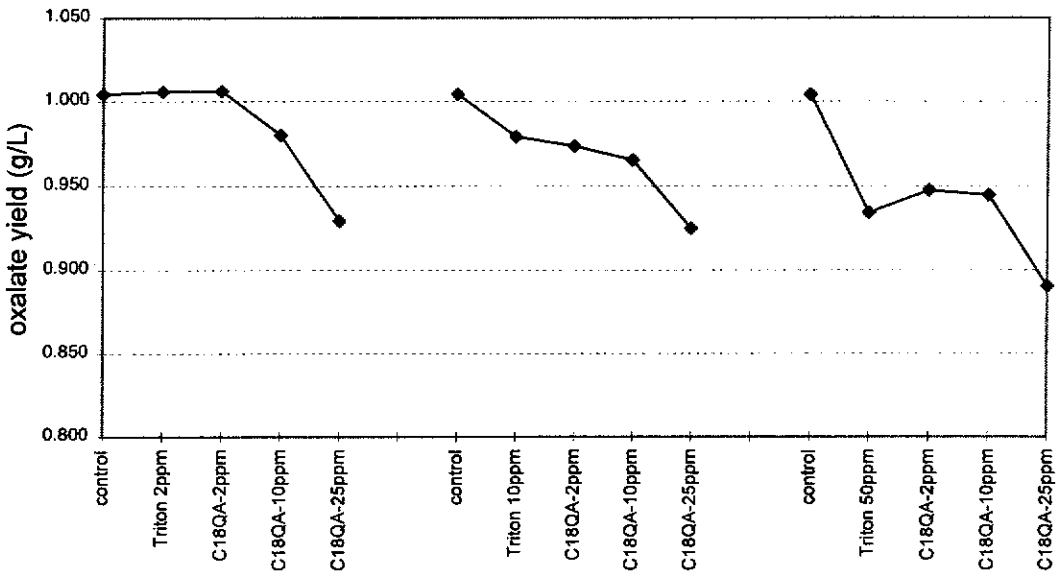

Figure 3.9: MOSPIT results of Triton X-100 on its own (2, 10 and 50 ppm) and in the presence of C18QA at different concentrations (2, 10 and 25 ppm)

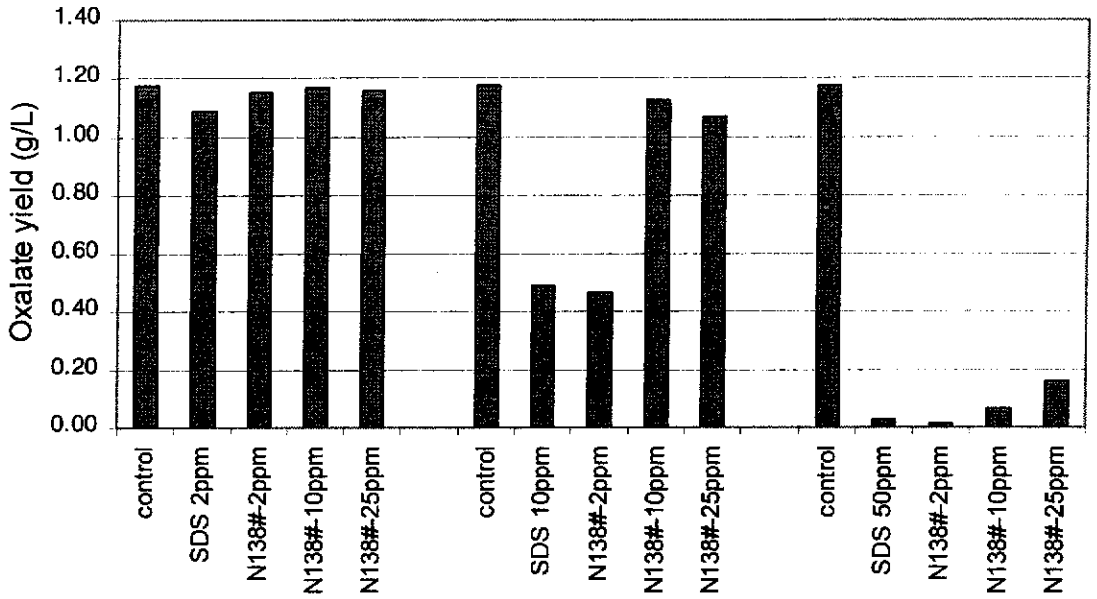

Figure 3.10: MOSPIT results of sodium dodecyl sulfate on its own (2, 10 and 50 ppm) and in the presence of N138# at different concentrations (2, 10 and 25 ppm)

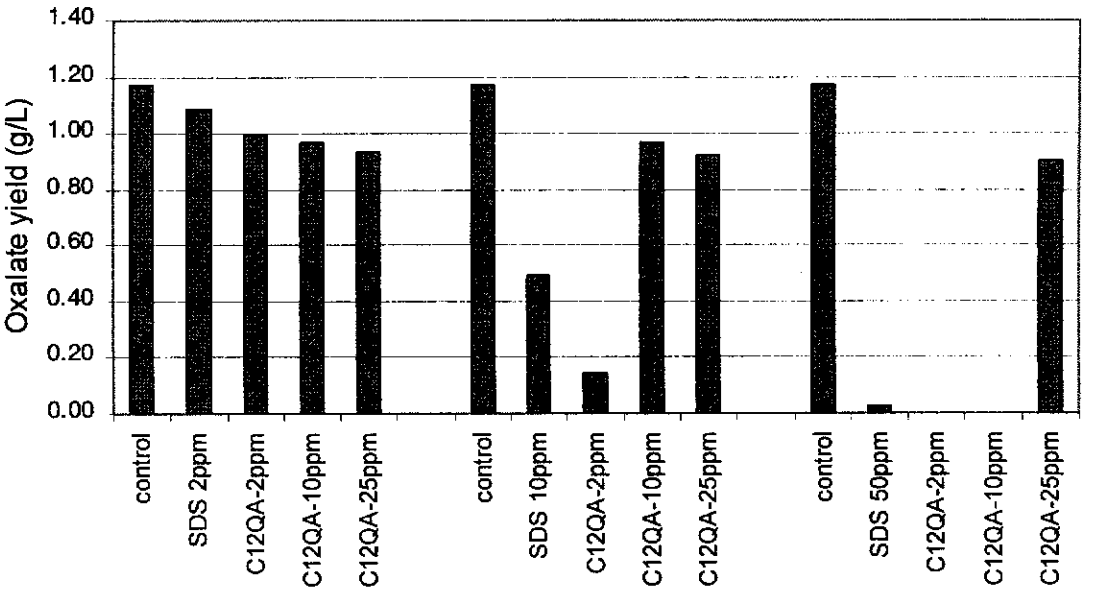

Figure 3.11: MOSPIT results of sodium dodecyl sulfate on its own (2, 10 and 50 ppm) and in the presence of C12QA at different concentrations (2, 10 and 25 ppm)

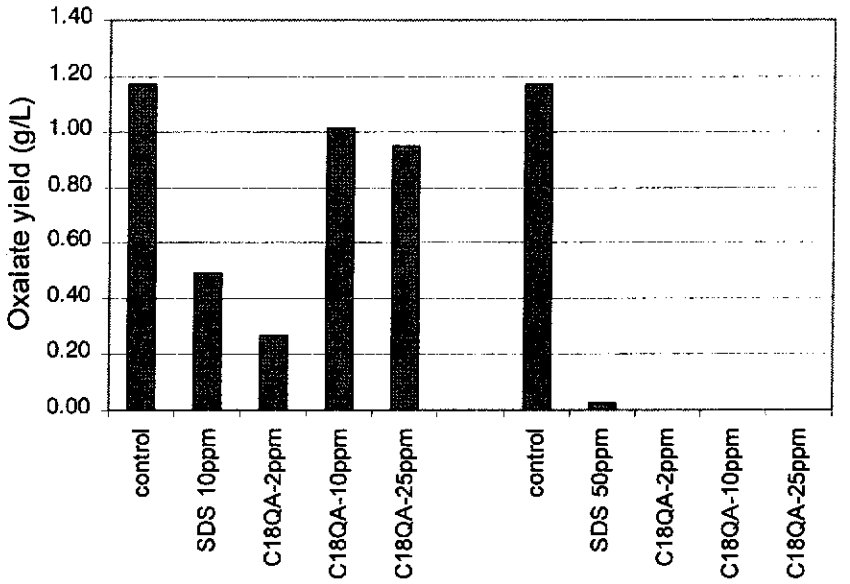

Figure 3.12: MOSPIT results of sodium dodecyl sulfate on its own (10 and 50 ppm) and in the presence of C18QA at different concentrations (10 and 25 ppm)

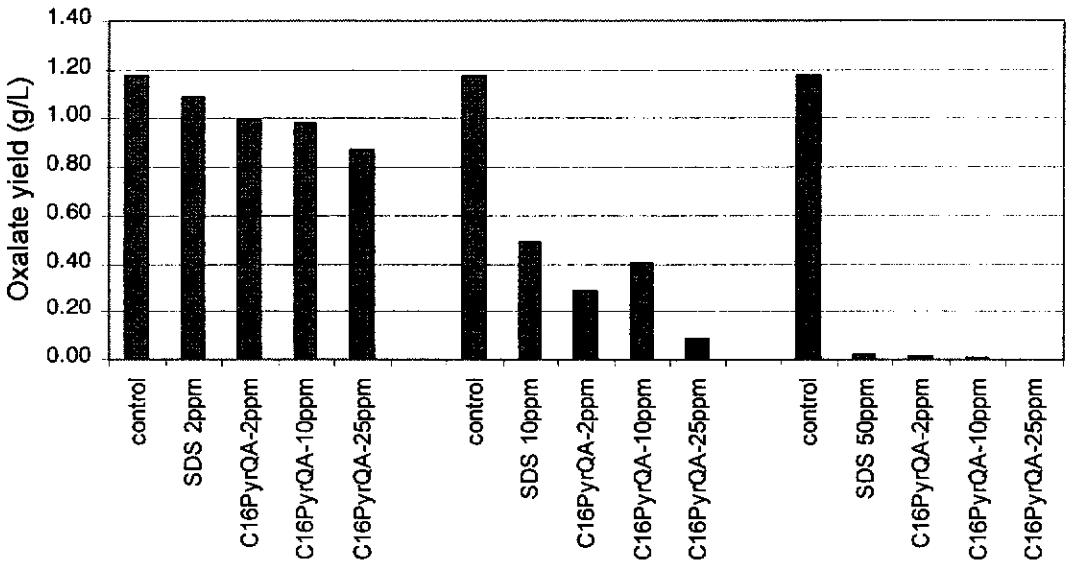

Figure 3.13: MOSPIT results of sodium dodecyl sulfate on its own (2, 10 and 50 ppm) and in the presence of C16PyrQA at different concentrations (2, 10 and 25 ppm)

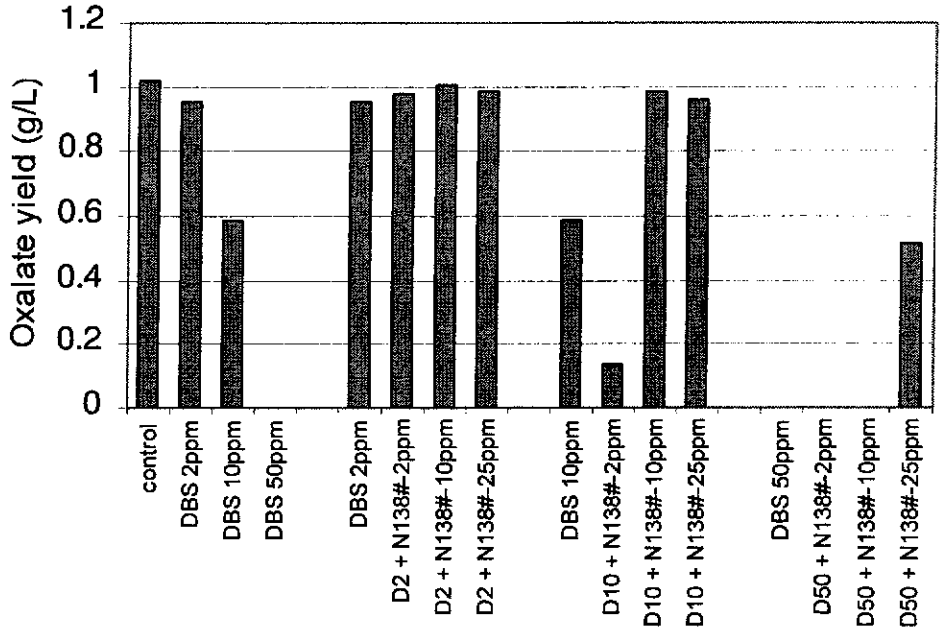

Figure 3.14: MOSPIT results of sodium dodecylbenzenesulfonate on its own (2, 10 and 50 ppm) and in the presence of N138# at different concentrations (2, 10 and 25 ppm)

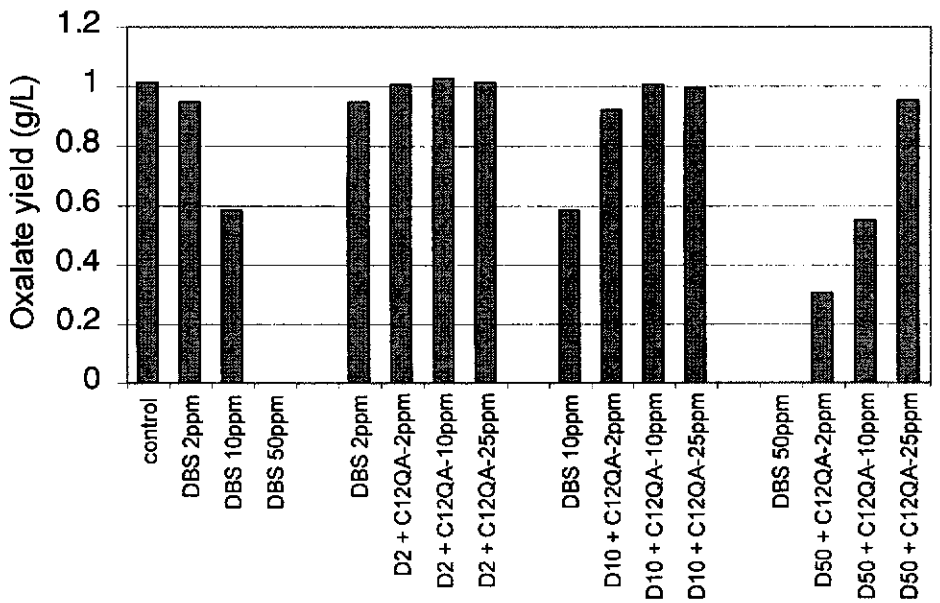

Figure 3.15: MOSPIT results of sodium dodecylbenzenesulfonate on its own (2, 10 and 50 ppm) and in the presence of C12QA at different concentrations (2, 10 and 25 ppm)

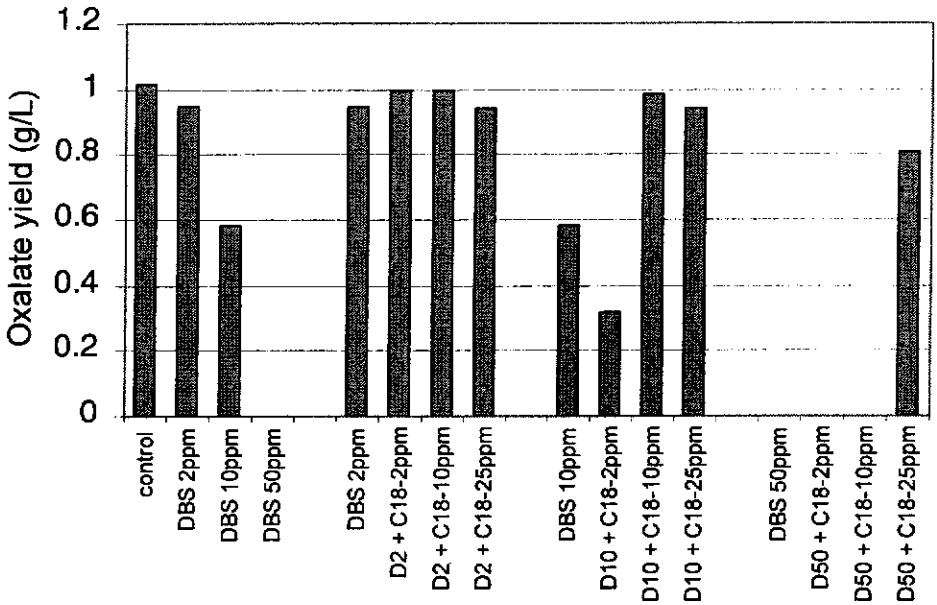

Figure 3.16: MOSPIT results of sodium dodecylbenzenesulfonate on its own (2, 10 and 50 ppm) and in the presence of C18QA at different concentrations (2, 10 and 25 ppm)

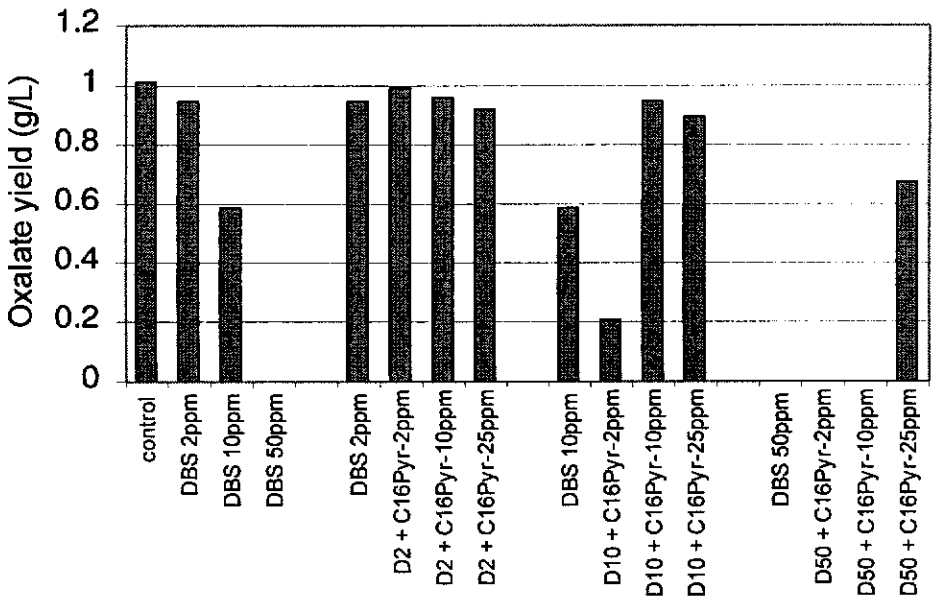

Figure 3.17: MOSPIT results of sodium dodecylbenzenesulfonate on its own (2, 10 and 50 ppm) and in the presence of C16PyrQA at different concentrations (2, 10 and 25 ppm)

The Triton X-100 non-ionic surfactant was found to be a weak oxalate poison. However, the presence of C18QA resulted in an additional effect on oxalate crystal

growth. No effect was found in the presence of C12QA, C16PyrQA or N138# (not shown).

The sodium dodecyl sulfate was a very efficient oxalate poison. The presence of QAs at low concentrations increased the inhibition (less yield), however, QAs at high concentrations (above their CMCs, see Section 1.4.3) decreased the inhibition, resulting in larger yields. High concentrations of QAs negated the inhibitory effect of sodium dodecyl sulfate. Presumably the QA, when it was present at high concentrations above its CMC, adsolubilises the sodium dodecyl sulfate in the micelles present in solution thereby preventing it from adsorbing on the oxalate surface.

Similarly, sodium dodecylbenzenesulfonate on its own was a very good oxalate poison. Small concentrations of QAs enhanced the inhibitory effect (2ppm of QA), however, high concentrations of QAs negated the inhibitory effect of sodium dodecylbenzenesulfonate.

It will be noted that the same behaviour was seen with the LMW plant extract, indicating that the components in the extract responsible for the synergistic effect with QAs might be anionic surfactants of small molecular weight.

3.3.7 Effect of QAs in synthetic liquor dosed with LMW-OSPs

LMW-OSPs are the components of the LMW cake extract identified by Alcoa so far. Their chemical compositions and concentrations in plant process liquor are commercially sensitive. Apart from testing some representative LMW-OSPs with the MOSPIT test, they can not be subjects of further investigation within this PhD work.

Using the MOSPIT test, it was decided to test some representative OSPs in order to determine which ones were necessary to make the QAs inhibit crystal growth in synthetic liquor (Figures 3.18-3.21).

The liquor was dosed with 10 ppm (if not marked otherwise) of one of the LMW-OSPs and 5 ppm of one of the following QAs: C12QA, C18QA, C16PyrQA or N138#. The effect of each LMW-OSP on its own was measured also.

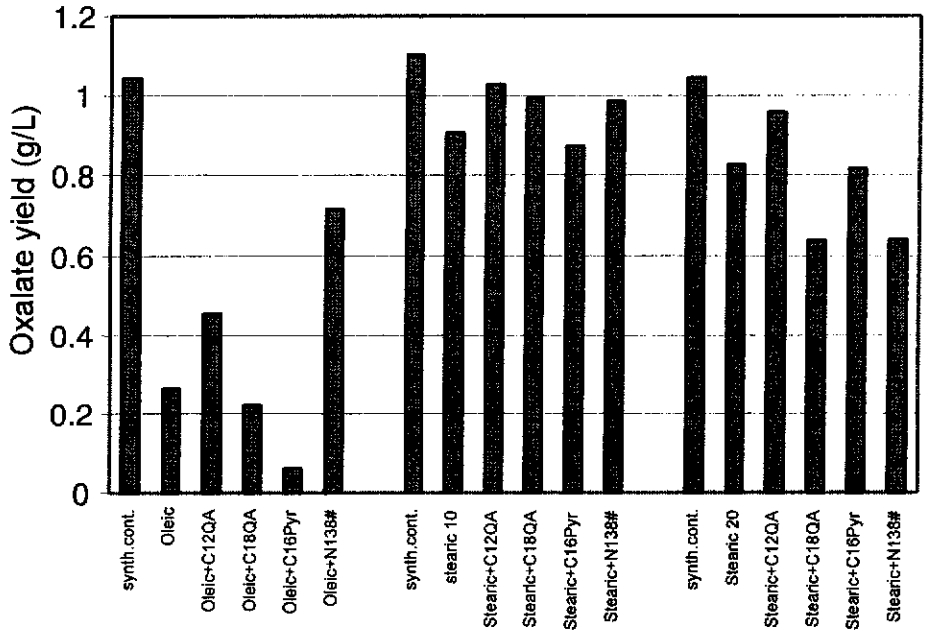

Figure 3.18: MOSPIT results of oleic acid (10 ppm) and stearic acid (10 or 20 ppm) and the effect of the addition of C12QA, C18QA, C16PyrQA or N138#

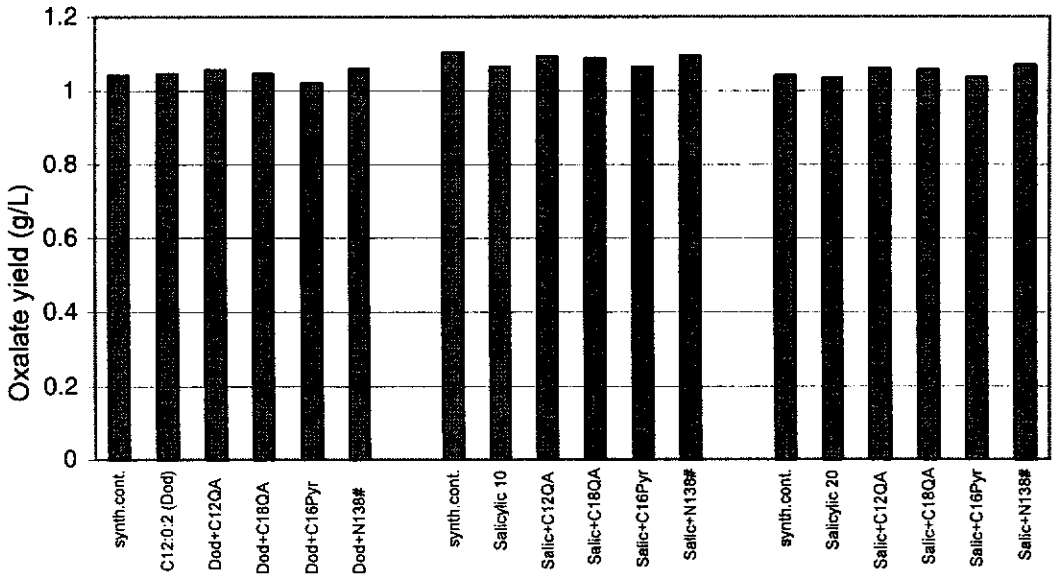

Figure 3.19: MOSPIT results of 10 ppm of dodecanedioic acid (C12:0:2) and of salicylic acid (10 or 20 ppm) and the effect of the addition of C12QA, C18QA, C16PyrQA or N138#

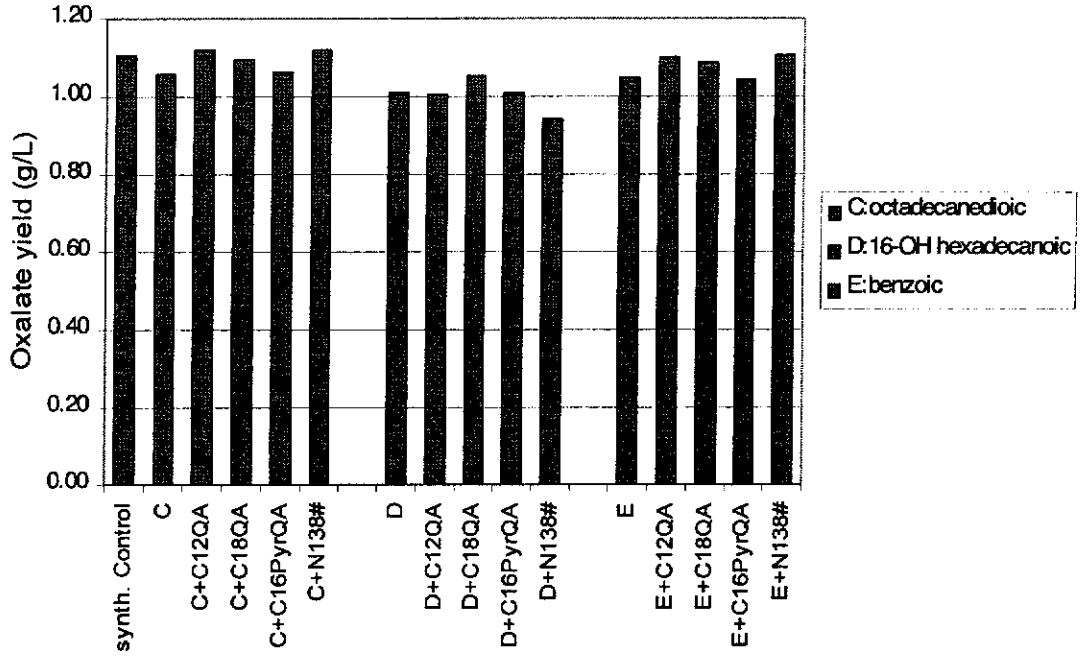

Figure 3.20: MOSPIT results of octadecanedioic acid, 16-OH hexadecanoic acid and benzoic acid (each at 10 ppm) and the effect of the addition of C12QA, C18QA, C16PyrQA or N138#

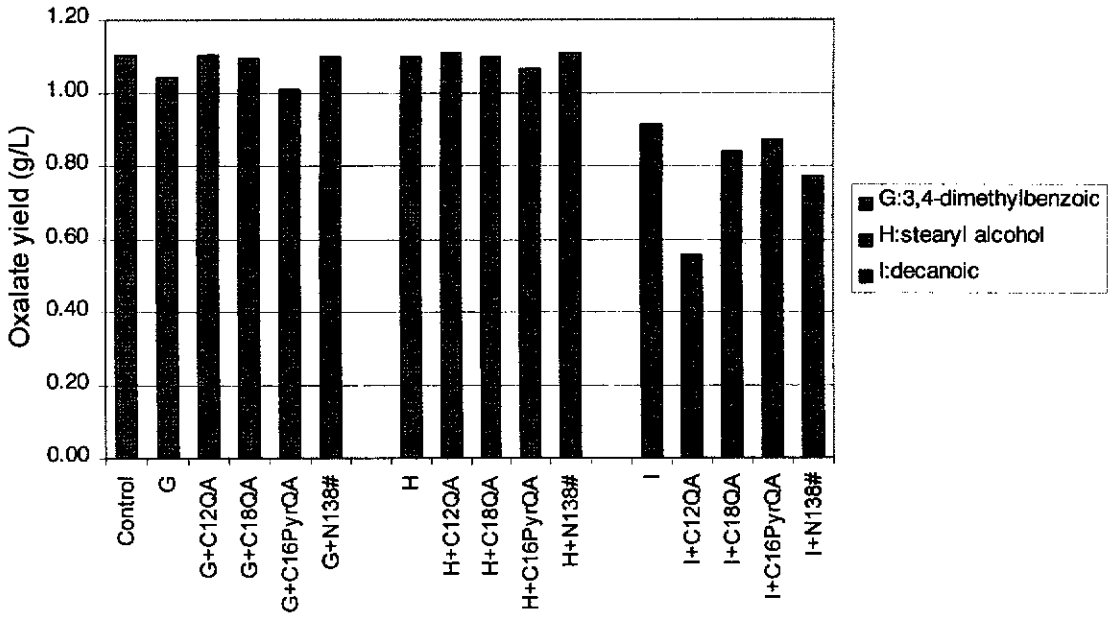

Figure 3.21: MOSPIT results of 3,4-dimethylbenzoic acid, stearyl alcohol and decanoic acid (each at 10 ppm) and the effect of the addition of C12QA, C18QA, C16PyrQA or N138#

Most of the compounds examined were ineffective at the concentrations employed in this study in synthetic liquor. Stearic, oleic and decanoic acids inhibited crystal growth of sodium oxalate. Synergy between oleic acid and C16PyrQA, stearic acid with C18QA or N138# and decanoic acid with C12QA was found. Table II contains the summary of the MOSPIT results of the LMW-OSPs and QAs in the presence of these chemicals in synthetic liquor.

TABLE II: Representative LMW-OSPs tested in MOSPIT test in synthetic liquor

	OXALATE POISON (10 ppm)		SYNERGY WITH SELECTED QAs (5 ppm of C12QA, C18QA, C16PyrQA or N138#)	
	YES	NO	YES	NO
Decanoic acid	+		+	
Stearic acid	+		+	
Oleic acid	+		+	
Benzoic acid		+		+
3,4-Dimethyl-benzoic acid		+		+
Dodecanedioic acid		+		+
1,18-Octadecanedioic acid		+		+
16-Hydroxy-hexadecanoic acid		+		+
Salicylic acid		+		+
Stearyl alcohol		+		+

3.4 Conclusions and Recommendations

3.4.1 Conclusions

Results confirmed that the presence of plant organics was essential to induce the inhibitory effect of QAs. Both the HUMIC and LMW extracts inhibited oxalate crystal growth in synthetic liquor. The decrease in yield was proportional to the concentration of organics. However, the addition of QAs into the liquor solution of these extracts resulted in enhanced crystal growth inhibition. In the presence of humates, the additional effect of QAs was proportional to the QA concentration and to the humate concentration. However, in the presence of LMW extracts, the high concentration of QAs often reversed the enhanced inhibitory effect of QAs found at low concentrations. This behaviour was confirmed with other anionic surfactant type compounds of low molecular weight.

Many of the tested non-Bayer chemicals (summarised in TABLES II & III) were found to be effective oxalate poisons at given concentrations. However, an enhanced inhibition of oxalate crystal growth in the presence of QAs was observed in a few instances only.

The commercial (non-Bayer) humics tested had an impact on oxalate yield, but the synergistic effect with QAs only appeared after the degradation of these materials at high temperature under liquor conditions. The degraded materials resulted in the same inhibitory effect at much higher concentrations than the non-degraded ones. The analysis of the humic liquor solutions before and after degradation did not show LMW contaminations at a significant level and the LMW concentrations did not change during the degradation. The chemical effects of the degradation on the commercial humics have not been identified.

Polyacrylate, sodium dodecyl sulfate, sodium dodecylbenzenesulfonate and Triton X-100 showed synergy with QAs.

Due to the confidential nature of the tested LMW-OSPs given in TABLE II, these compounds and the LMW extract was not investigated further within the PhD project. Synergy between decanoic acid and C12QA, oleic acid and C16PyrQA, stearic acid and C18QA or N138# were found.

From the results measured to date, desired features of the organics that will interact with QAs to produce an enhanced inhibitory effect can be concluded.

a) The organics have to be oxalate poisons. Without exception, all of the organics that showed synergy with QAs inhibited crystal growth of sodium oxalate on their own.
b) The surfactant nature of the organics seems to be crucial. Having other characteristics, such as high molecular weight, similar functional groups as humates were not enough to induce the action of QAs.

3.4.2 Recommendations

The synergy found between plant organics and QAs is quite interesting. QAs behave differently in the presence of different extracts. The fulvic plant and cake extracts have not been investigated, and neither has the mixture of extracts.

The nature of interaction between QAs and plant organics is not clear. More work would be required for a better understanding of the attraction between QAs and plant organics in liquor solutions.

Another interesting question is how the excess of these extracts in plant liquor would affect the action of QAs. When the ratio of fractions of plant organics is unbalanced, QAs might give a response different from that measured in synthetic liquor.

These questions are beyond the scope of this work; nevertheless, further investigations would lead to a better knowledge of the role of plant organics in the process and of the action of QAs in different types of liquors.

Chapter 4

Analysis of C18QA

4.1 Introduction

It was thought that the inhibition of crystal growth of sodium oxalate measured in the presence of certain organics and QAs was probably due to the adsorption of these chemicals onto the oxalate surface. Hopefully, knowing the adsorption behaviour of QAs and organics under different conditions at a molecular level would lead us to understand the inhibitory effect of QAs and organics measured macroscopically.

It was planned, as part of the original proposal, to measure adsorption isotherms of QAs on sodium oxalate in synthetic liquor, and for this, it was necessary to be able to measure concentrations of QAs in liquor. The strongest crystal growth inhibitor was found to be C18QA; consequently, it was decided to examine the adsorption character of this surfactant in detail. Accordingly, the analysis method had to be suitable specifically for the analysis of this surfactant.

A method developed by Hind, Bhargava & Grocott (1997a) for the determination of QAs (C12QA, C14QA and C16QA) in liquor samples was employed. Preliminary laboratory tests showed that this method was suitable for the analysis of C18QA as well. The method was adopted, tested for C18QA analysis, improved and modified for the determination of C18QA on solid oxalate.

4.2 Experimental

4.2.1 Materials

Chemicals: Analytical reagents, n-eicosane ($C_{20}H_{40}$, 99%) and n-docosane ($C_{22}H_{46}$, 99%) were purchased from Sigma-Aldrich Pty Ltd. Mannitol (99%) from BDH Chemicals, hydrochloric acid (HCl, 36% solution) from Rhone-Poulenc, anhydrous sodium sulfate (Na_2SO_4, 99.5%) and potassium iodide (KI, 99.5%) from Sigma Chemicals, and organic solvents dichloromethane (99.5%), chloroform (99%)

and methanol (99.8%) were obtained from Rowe Scientific. Alcoa World Alumina-Australia, Kwinana, supplied dimethylformamide and 1,1,2-trichloroethane solvents. Tertiary amines $C_{12}H_{25}N$ $(CH_3)_2$, $C_{13}H_{27}N(CH_3)_2$, $C_{16}H_{33}N(CH_3)_2$ and $C_{18}H_{37}N(CH_3)_2$ were obtained from Kasei Chemical Company. All other chemicals used were of analytical grade.

4.2.2 Instrumental

An HP 5890 Series II plus gas chromatograph (Hewlett-Packard) equipped with an HP767 automatic injection system (Hewlett-Packard) and FID detector was employed. A DB-5MS fused silica capillary column (length: 50 m; ID: 0.2 mm; film: 0.33 μm) was employed.

4.3 Results and Discussions

4.3.1 The original method

A method was developed for the quantitation of C12QA, C14QA and C16QA in liquor solutions (Hind, Bhargava & Grocott 1997a). The method consists of the extraction of the quaternary amine iodide salt with dichloromethane, then the salts are thermally decomposed by high temperature in the injector port of the GC to produce tertiary amines (TAs) which are amenable to GC analysis. The QAs (through the TAs) are then quantified by calibration standards. The procedure employed the following steps:

1) Dilution of 5 mL liquor sample containing QA compounds with 10 mL of deionised water.
2) Addition of 2.5 g mannitol to complex the aluminate ion.
3) Addition of 2.25 mL of 5 M HCl solution to adjust the pH to 10-12.
4) Addition of 4.5 g KI.
5) Addition of 12 mL dichloromethane containing eicosane internal standard.
6) Mechanical shaking to extract the QA-iodide ion pair into the organic phase (10 min).
7) Separation and drying of the organic phase over Na_2SO_4.
8) Evaporation to dryness (40 °C <10 mbar).
9) Storage in 500μL methanol.

10) Injection of the sample into the GC-FID port (300 °C) which resulted in the transformation of ion pairs into the tertiary amine analogues.
11) Identification of peaks comparing the retention times of the samples to those of a mixture of known TAs.
12) Quantification of QAs based upon the standard/ internal standard peak area ratios

The procedure was characterised with a 2-4 RSD% injection precision (from repeated injections), 7-10 RSD% extraction precision and a 0.05 μg limit of detection. The method measured typical QA concentrations between 0-10 ppm. The authors of the original paper reported low recovery and non-linear calibration curves for higher concentrations of QAs.

4.3.2 Improvement of the method

Preliminary laboratory tests showed that this method was suitable for the analysis of C18QA. Some work had been done to improve the method in the laboratories of Alcoa before this PhD project commenced. The changes were as follows:

1) Sample volume changed to 2 mL, dilution with 20 mL of deionised water.
2) Three internal standards were added into the samples: C13TA and $C_{22}H_{46}$ dissolved in dichloromethane, and C14QA.
3) Addition of 2.0 g mannitol to complex the aluminate ion.
4) Addition of 1 mL of 5 M HCl solution to adjust the pH to 10-12.
3) Addition of 9.0 g KI.
4) Addition of 18 mL dichloromethane.
5) Sample storage in 500μL dichloromethane.

Calibration standards (0 – 16 ppm) of C13TA, $C_{22}H_{46}$, $C_{20}H_{42}$, C14QA, C16QA and C18QA were prepared and used in the modified method to test the precision of the determination. The errors calculated from the repeated injections of the samples or the replicate sample preparations are given in Table IV.

TABLE IV: Precision of C18QA determination

Analyte	Errors Analyte/$C_{22}H_{46}$ peak area ratios (RSD%)	
	Replicate injections	Replicate analyses
C13TA	2.2	7.6
$C_{20}H_{42}$	2.2	6.5
C14QA	2.5	7.5
C16QA	2.6	7.3
C18QA	3.6	10.6

This method was found to be suitable for the determination of C18QA. Further investigations were carried out to clarify the sources of the errors and to further improve the recent method. Tests showed that it was difficult to improve the analysis any further. Parameters, such as different filter materials (GFA glass or Whatman paper), GC port temperature (250-300 °C), or the pH of the samples (5-12) did not alter the precision of the analysis.

A problem regarding the storage of samples arose during the investigations. This difficulty was solved successfully. The TAs were found to be unstable in dichloromethane. Organic solvents, such as methanol, chloroform, dimethyl-formamide and 1,1,2-trichloroethene were tested, and chloroform was chosen as being the best solvent for storing the samples. The chromatograms obtained with this solvent exhibited sharp peaks without tailing.

4.3.3 Analysis of C18QA in liquor samples

Synthetic liquor solutions of 3, 5, 8, 10 and 16 ppm of C18QA standards were made up in duplicate and samples were prepared with the method described above for GC-FID analysis. These concentrations involved the run of 12, 20,32, 40 and 64 ng of C18QA with the GC-FID. C16QA and $C_{20}H_{42}$ eicosane were employed as internal standards. Figure 4.1 shows the peak area ratios between C16QA and $C_{20}H_{42}$ and C18QA and $C_{20}H_{42}$.

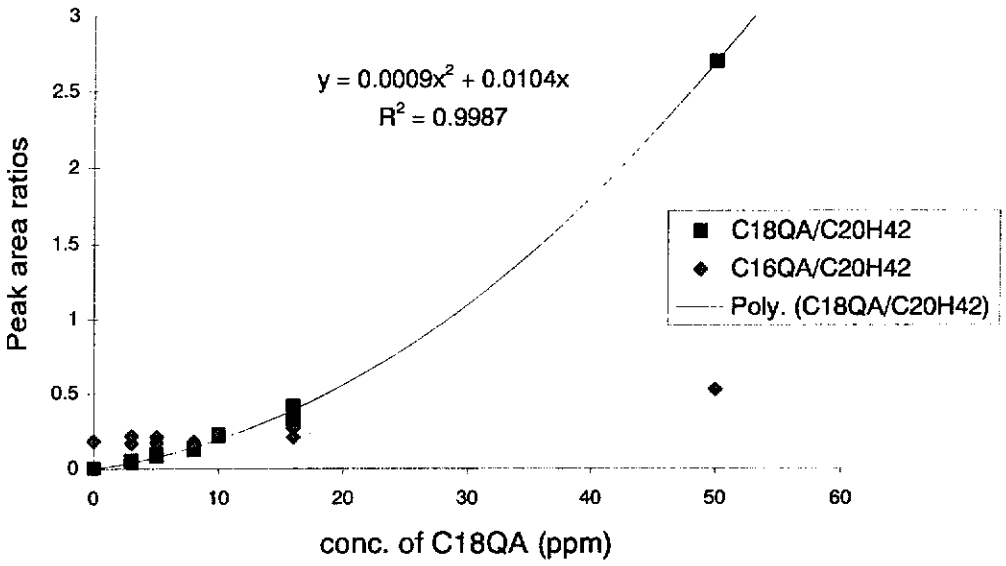

Figure 4.1: Peak area ratios between: (a) C16QA and $C_{20}H_{42}$ internal standards; (b) C18QA and $C_{20}H_{42}$ internal standard

Results show that the peak area ratios between QAs and $C_{20}H_{42}$ did not result in linear responses. The non-linearity indicates some losses of QAs at low concentrations. This is probably due to the adsorption of QAs during the filtration of samples and adsorption on GC parts. The $C_{20}H_{42}$ obviously has less affinity than the QAs towards the surface adsorption. Figure 4.2 shows that the ideal internal standard for the determination of C18QA is the C16QA.

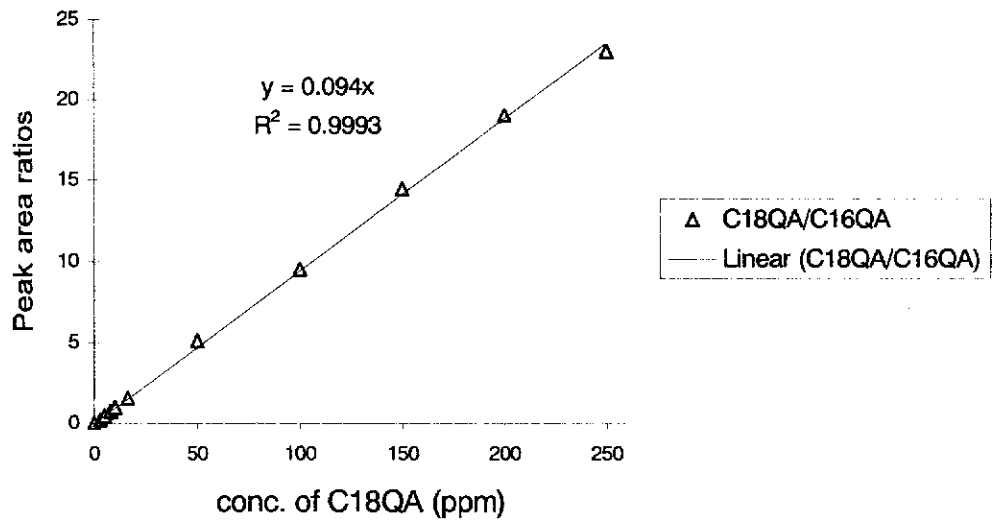

Figure 4.2: Peak area ratio between C18QA and C16QA internal standard

The C16QA internal standard has a structure very similar to the analyte, and the two QAs behave the same way along the procedure. Consequently, the peak area ratio between C18QA and C16QA gives a linear calibration curve up to very high concentrations (250 ppm, run of 1000 ng). The linear calibration curve up to high concentrations enabled us to avoid subsampling during the adsorption measurements, which had caused large errors.

In the end, the procedure used for the analysis of C18QA in liquor during this study was as follows:

1) Dilution of 2 mL liquor sample containing C18QA with 20 mL of deionised water.
2) Two internal standards were added into the samples: C16QA and $C_{20}H_{42}$.
3) Addition of 2.0 g mannitol to complex the aluminate ion.
4) Addition of 1 mL of 5 M HCl solution to adjust the pH to 10-12.
5) Addition of 9.0 g KI.
6) Addition of 18 mL dichloromethane.
7) Mechanical shaking to extract the C18QA-iodide ion-pair into the organic phase (20 min).
8) Separation and drying of the organic phase over Na_2SO_4.
9) Evaporation of the organic phase to dryness.
10) Dissolution of the residue and storage in 1000μL dichloromethane.
11) Injection of the sample into the GC-FID port (250 °C) which resulted in the transformation of the ion pairs into the tertiary amine analogues.
12) Identification of peaks comparing the retention times of the samples to those of a mixture of known TAs.
13) Quantification of C18QA based upon the standard/ internal standard peak area ratios

Although the precision of the determination of C18QA could not be improved further, and the error of the analysis remained 7-10 RSD% at the concentration of 8 ppm of C18QA, the significant achievement was that the calibration curve became

linear up to 250 ppm (run of 1000ng) of C18QA using the ratio between C18QA and C16QA internal standard.

4.3.4 Analysis of C18QA on solid sodium oxalate

The generation of adsorption isotherms involved the determination of the amount of C18QA adsorbed on the solid oxalate. This amount can be deducted from the analysis results of the liquor samples or can be measured directly. It was decided to determine the adsorbed C18QA directly by analysis. Accordingly, the method used for the determination of C18QA in liquor samples had to be modified.

The solid oxalate samples were dissolved in water. As the pH of the samples was already between 8-10, the solutions did not need any acidification. The samples did not contain aluminate, and so the addition of mannitol was unnecessary and was simply left out. Calibration standards of 10, 20, 30, 40 and 50 ppm of C18QA were made up in 10 g/L sodium oxalate solution (calculated pH=8.5) and prepared for GC-FID. These concentrations involved the run of 40, 80, 120, 160 and 200 ng of C18QA on the GC-FID. Figure 4.3 shows the ratios between C18QA, C16QA and $C_{20}H_{42}$ peak areas obtained from the chromatograms as a function of C18QA concentration.

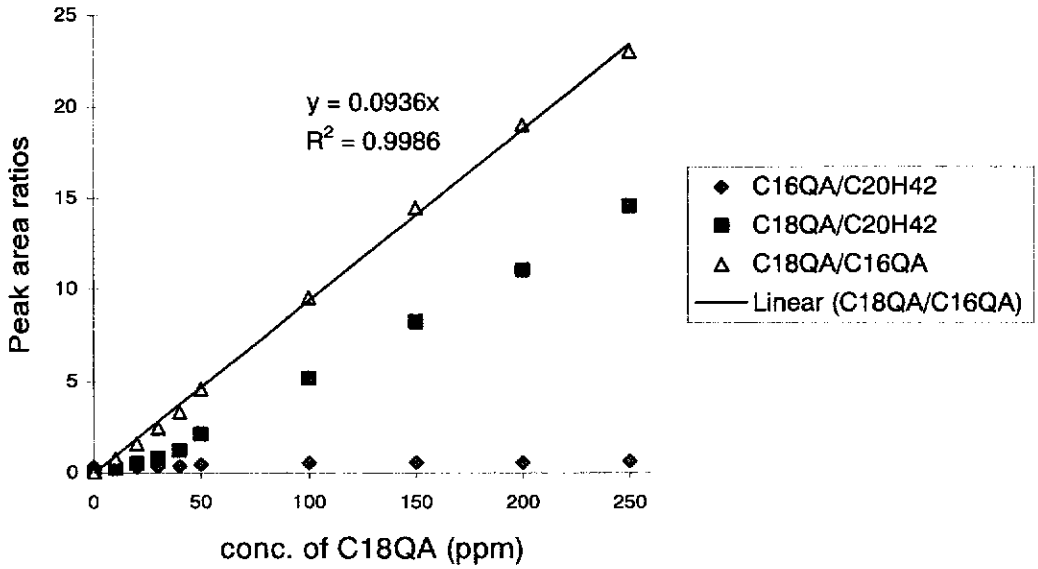

Figure 4.3: Peak area ratios between C16QA and $C_{20}H_{42}$ internal standards, between C18QA and $C_{20}H_{42}$ internal standard and between C18QA and C16QA internal standard prepared from sodium oxalate solution

A linear calibration curve is obtained up to 1000 ng of C18QA using the ratio between C18QA and C16QA internal standard. During this study, the method used for the analysis of C18QA adsorbed on solid oxalate consisted of the following steps:

1) Dissolution of solid oxalate samples containing C18QA with 20 mL of deionised water.
2) Two internal standards were added into the samples: C16QA and $C_{20}H_{42}$.
3) Addition of 2.0 g mannitol to complex the aluminate ion.
4) Addition of 9.0 g KI.
5) Addition of 18 mL dichloromethane.
6) Mechanical shaking to extract the C18QA-iodide ion-pair into the organic phase (20 min).
7) Separation and drying of the organic phase over Na_2SO_4.
8) Evaporation of the organic phase to dryness.
9) Dissolution of the residue and storage in 1000μL dichloromethane.
10) Injection of the sample into the GC-FID port (250 °C) which resulted in the transformation of the ion pairs into the tertiary amine analogues.
11) Identification of peaks comparing the retention times of the samples to those of a mixture of known TAs.
12) Quantification of C18QA based upon the standard/ internal standard peak area ratios

Repeated extraction procedures indicated that the error of the determination was 7-10 RSD%.

4.4 Conclusions and Recommendations

4.4.1 Conclusions

A method was developed in 1997 for the quantitative analysis of quaternary amines from liquor solutions. The same procedure was found to be suitable for C18QA analysis.

While low recovery and non-linear calibration curves at concentrations above 5 ppm were reported in the original method, significant improvement of the method was achieved. With the addition of an internal standard very similar chemically to

the analyte, the calibration curve became linear up to 250 ppm (1000 ng). That enabled the elimination of a sub-sampling step in adsorption isotherm measurements.

The method was modified in order to analyse C18QA from sodium oxalate solutions with pH much lower than in liquors. With this modified method, determination of C18QA adsorbed on the surface of solid oxalate was directly obtained.

Significant improvement was achieved regarding the storage of samples. As the TAs were found to be unstable in dichloromethane, other solvents were tested. Chloroform was found to be suitable for storage and as a carrier for the GC-FID.

Although attempts were made, it was very difficult to improve the precision of the method any further. The standard deviation was determined to be 7-10 % for concentrations between 0-20 ppm.

4.4.2 Recommendations

An attempt was made to apply the conditions developed above for the determination of other QAs, such as C12QA, C16PyrQA or N138#. It was evident from the results that the same conditions could not be used for the analysis of those QAs. For instance, N138# did not give any signal on the GC-FID. It seems that the optimum conditions for the analysis of QAs should be worked out individually in any future work.

Chapter 5

Quaternary Amines Dissolved in Synthetic Liquor; Critical Micelle Concentration Measurements

5.1 Introduction

The adsorption isotherm at a solid/liquid interface represents the amount of adsorbate adsorbed on a unit of surface of the adsorbent as a function of the concentration (activity) of the adsorbate in solution (section 1.3). Then, every process that influences the surface concentration or the concentration of adsorbate in solution affects the adsorption isotherm. The surface concentration can be affected by, for instance, the presence of another adsorbate competing for the surface. The concentration of adsorbate in solution can be changed, usually decreased, by processes, such as protonation, ion-association, complexation or, in the case of surfactants, micelle formation (section 1.4.3). Because the adsorption isotherm function is valid for activities, the adsorption isotherm can be affected through the activity coefficient with ionic strength.

Dealing with surfactants, the most obvious process affecting the surfactant concentration in solution is micelle formation. The CMC (critical micelle concentration) is a significant point on the adsorption isotherm. This point represents the concentration above which micelles exist in solution. Usually, there is a knee in the adsorption isotherm at this concentration, due to the fact that the concentration of monomer surfactants in solution remains constant above the CMC.

5.2 Experimental

5.2.1 Instrumental

CMCs were obtained using surface tension measurements carried out using an Analite Surface Tension Meter (Selby Scientific) and Marienfeld plates. The

CMCs were determined from the plot of the surface tension of liquor versus the surfactant concentration.

5.2.2 Conditions

Synthetic liquor was saturated with sodium oxalate at 60 °C, purified with activated carbon and filtered. 100 ml of liquor was conditioned at 60 °C in a jacketed vessel connected to a water bath and dosed with different volumes of a stock solution of C18QA. The surface tension of the liquor was measured with the plate method.

5.3 Results and Discussions

5.3.1 CMC of C18QA

Figure 5.1 shows the surface tension of liquor as a function of the C18QA concentration. The CMC was determined from the plot, and it was found to be reproducible. The CMC of C18QA determined from the data was 1.5 ppm.

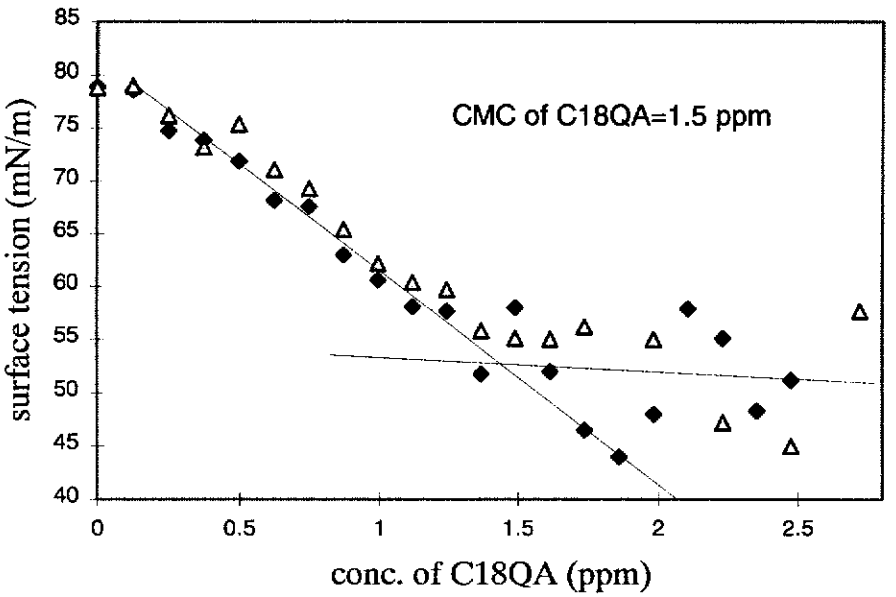

Figure 5.1: The surface tension of synthetic liquor as a function of C18QA concentration at 60 °C. Duplicate measurement.

5.3.2 Surface activity of QAs in different liquors

The behaviour of QAs in liquor was measured through surface tension measurements. It was quite surprising that the CMC of QAs varied with the

composition of liquors. Figure 5.2 shows the surface tension of different liquors as the function of N138# concentration.

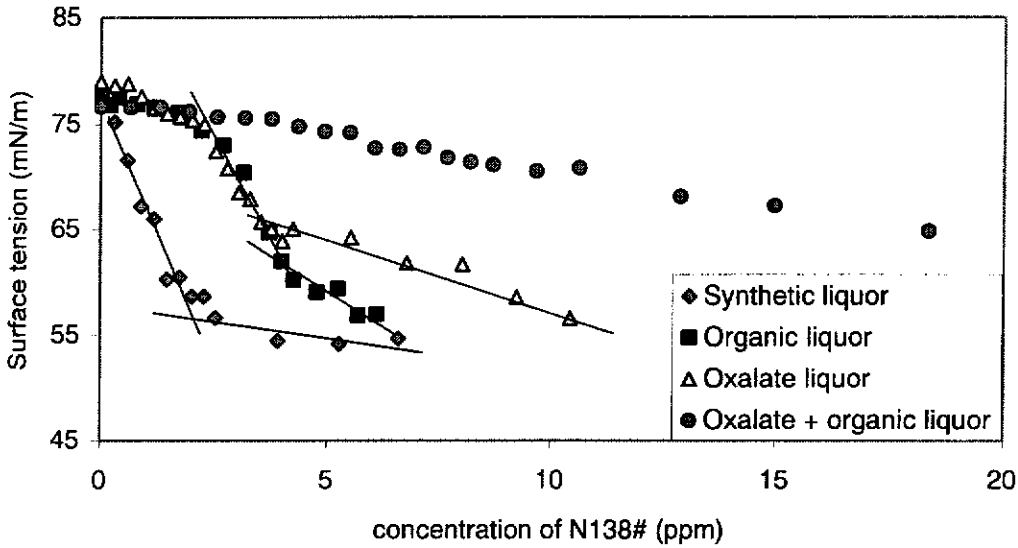

Figure 5.2: The surface tension of different liquors as the function of N138# concentration at 60 °C.

The synthetic liquor in this experiment was prepared without the addition of sodium malonate and sodium succinate (see section 2.2.3). When this liquor was saturated with sodium oxalate (Oxalate liquor) or the liquor contained the appropriate amount of sodium malonate and sodium succinate (Organic liquor), the CMC was different. In liquor containing sodium oxalate, sodium malonate and sodium succinate (Oxalate + organic liquor), the CMC could not be determined. The surface tension did not change the expected way when N138# was added. These results show clearly that an interaction exists between QAs and di-carboxylates in liquor.

The ionic strength of the liquor has an effect on the CMC measured. The higher the ionic strength is, the lower the CMC. The variation in total sodium in these measurements was small, 4.75%. The increase in CMC measured can not be the result of an increase in ionic strength, as the change is very significant, three times higher, and it shows a parallel trend with the total sodium.

The CMC of QAs varied not only with the liquor composition, it also varied with the concentration of the components. Figure 5.3 represents the CMCs

measured in liquors containing different oxalate concentrations. The CMC of N138# increased with increasing oxalate concentration in liquor. This implies that some of the quaternary amines were bound by the oxalate ions in liquor. Micelles are formed when a certain free ion-concentration is reached. In liquors of high concentration of oxalate, more QA was needed to achieve the same concentration of free molecules.

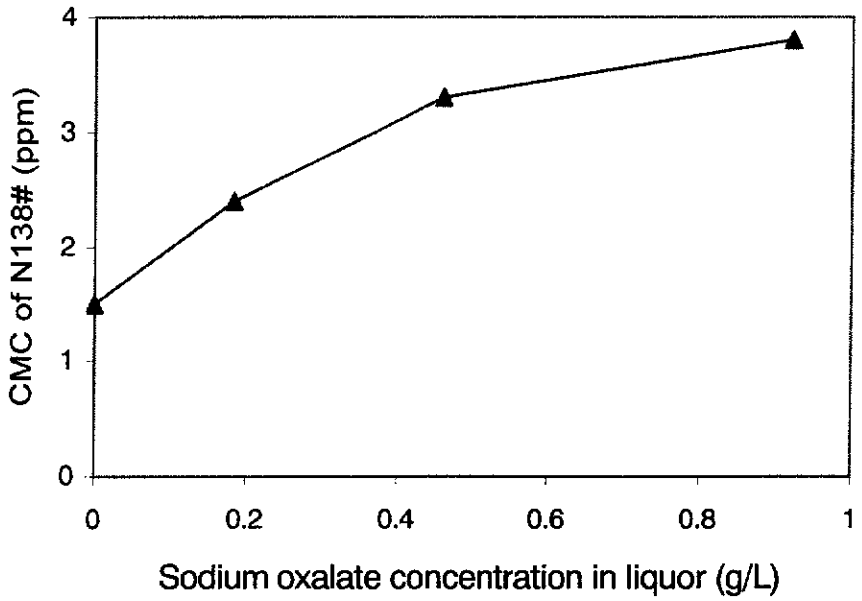

Figure 5.3: The CMC of synthetic liquor containing N138# with different oxalate concentrations

5.4 Conclusions and Recommendations

5.4.1 Conclusions

The primary aim of surface tension measurements was to determine the CMC of C18QA for the interpretation of the adsorption isotherm of this quaternary amine. The CMC of C18QA that was determined from the surface tension vs. surfactant concentration plot was 1.5 ppm in liquor containing 0.722 g/L sodium oxalate, 5 g/L sodium malonate and 15 g/L sodium succinate.

The effect of QAs other than C18QA on the surface tension of liquor was investigated for comparison. It was evident from the measurements that an interaction exists between QAs and the di-carboxylate components of the

synthetic liquor. This interaction is probably due to the very high ionic strength of the solution. Calculations show that the amount of water in synthetic liquor is not sufficient to form entire hydrate cells around the ions, therefore, ion-associations are highly favoured in this solution. Unfortunately, further investigation of this phenomenon was not possible within this project.

5.4.2 Recommendations

Results revealed that the CMC of QAs in liquors depended on the composition of synthetic liquor. It was not only the ionic strength that influenced the CMC, for example as in diluted solutions, specific anions had direct interactions with quaternary amines. It is recommended that the CMC of QAs should be given together with the exact composition of the liquors in the future. Especially, the sodium oxalate, sodium malonate and sodium succinate components seem to be crucial.

Chapter 6

Adsorption Isotherm Measurements on Sodium Oxalate in Synthetic Liquor

6.1 Introduction

It was found that QAs inhibited oxalate crystal growth in plant liquors and in synthetic liquors in the presence of certain organics. The effect of QAs measured macroscopically certainly has an explanation at a molecular level. It was thought that adsorption measurements could lead to an understanding of the mechanisms by which QAs affect oxalate crystallization.

It was decided to develop an adsorption technique to measure adsorption isotherms from synthetic liquor. The procedure had to be suitable for adsorption measurements at 60 °C on acicular sodium oxalate, to be relevant to plant operation.

The strongest crystal growth inhibitor was found to be the C18QA; consequently, this surfactant was chosen for a detailed examination of its adsorption character. Since it was shown that plant organics were necessary for the action of QAs, and the humic material was especially effective in this role, it was decided to measure the adsorption behaviour of the HUMIC cake extract as well. It was planned to measure the adsorption isotherms of both, the C18QA and HUMIC cake extract individually and from a mixture of the C18QA and the HUMIC cake extract.

6.2 Experimental

6.2.1 Materials

Chemicals: C18QA (see section 2.2.1); HUMIC cake extract (see section 3.2.3).

Adsorbent: acicular sodium oxalate (see section 2.2.1).

Background liquor: synthetic liquor saturated with sodium oxalate (see section 2.2.3)

6.2.2 Analysis

C18QA concentrations in liquor and on the solid oxalate surface were determined with the method given in Chapter 4.

HUMIC cake extract concentrations in synthetic liquor were determined using an HP 8453 UV-VIS spectrophotometer (Hewlett-Packard). Absorbances of the HUMIC cake extract in liquor solutions were determined using a 1 cm or 10 cm pathlength cuvette to record the spectra in the range of 290-560 nm.

CMCs (critical micelle concentrations) of the HUMIC cake extract and C18QA were obtained using surface tension measurements outlined in Chapter 5.

Degree of agglomeration of solid sodium oxalate was measured with Focus Beam Reflection Measurement using a Lasentec M500.

Calcium concentrations were determined using Perkin Elmer Optima 3000 ICP.

6.2.3 Conditions

Temperature: All of the adsorption isotherm measurements were carried out at 60 °C.

Synthetic liquor was used as matrix solution (see section 2.2.3).

6.2.4 Procedure

An adsorption isotherm procedure for C18QA and HUMIC cake extract was developed. The synthetic liquor was saturated with sodium oxalate, purified with activated carbon at 60 °C and filtered. Liquor (10.0 mL) in glass culture tubes was conditioned with 5 g/L acicular sodium oxalate for one hour at 60°C in a rotating water bath. The liquor was dosed with different volumes of a stock solution of the adsorbate. After 20 hours adsorption time, which was found to be sufficient to reach equilibrium, the tubes were centrifuged at 60 °C for 10 minutes and the liquor decanted into another tube for analysis. After decanting the liquor, the remaining solid in the original tube was dissolved with water and the adsorbate content determined. The liquor remaining on the solid oxalate was weighed and taken into account.

6.3 Results and Discussions

6.3.1 Stability of the HUMIC cake extract

It is known that the humic material degrades continuously under plant conditions. The rate of degradation has not been determined in different parts of the process. An important condition for adsorption isotherm measurements is that the adsorbate should remain unchanged during the adsorption period. So, it was necessary to measure the stability of the HUMIC cake extract.

Liquor solutions of 2, 4, 6, 8 and 10 mL/L of HUMIC cake extract were made up and kept at 60 °C for 5 days. The absorbances of solutions between 290-560 nm were measured from time to time. Figure 6.1 shows that the absorbance of the humic liquor solutions, for instance measured at 410 nm, did not change for 5 days, indicating that the extract was stable in liquor during the time in which adsorption experiments were carried out (normally 20 hours).

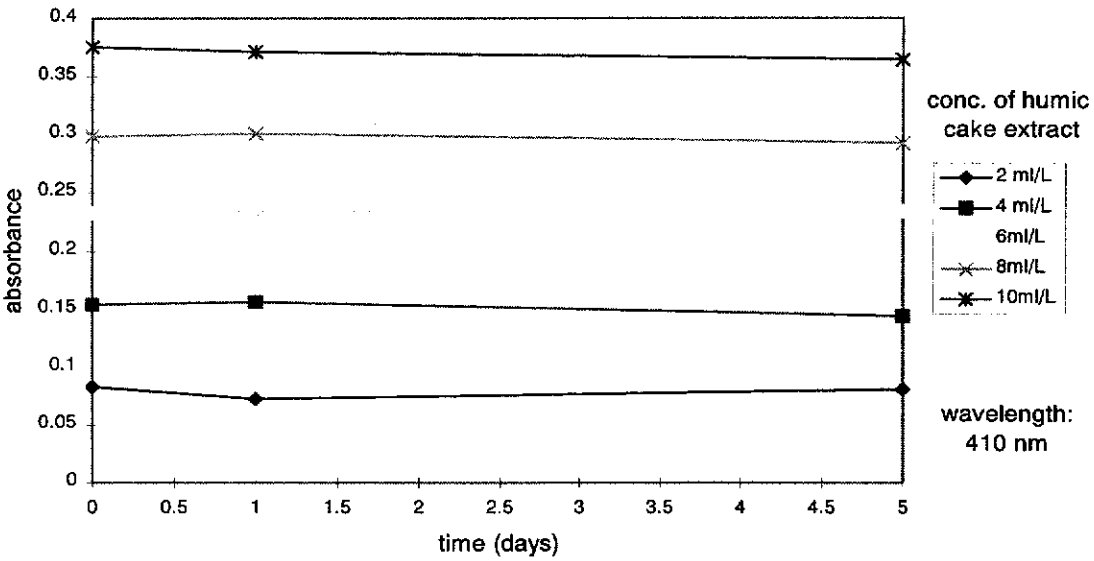

Figure 6.1: A plot of measured humic absorbance versus equilibration time.

6.3.2 Determination of the sufficient adsorption time

MOSPIT tests showed that QAs were only effective growth inhibitors in the presence of plant organics. It was therefore decided to measure C18QA and HUMIC cake extract adsorption individually and from a mixture of these two components. Accordingly, the sufficient adsorption time to reach equilibrium of

adsorbate between the surface and the solution had to be determined for the mixture. That adsorption time should be sufficient for the individual components as well.

Adsorption kinetics for C18QA and HUMIC cake extract were then measured after simultaneously adding the C18QA and HUMIC cake extract into the synthetic liquor at the following concentration ratios: 5ppm QA/5 mL/L extract, 25ppm QA/5 mL/L extract and 25ppm QA/25 mL/L extract. Adsorption measurements were made at various times between 17 hours and 3 days. Figure 6.2 shows that the equilibrium for C18QA and HUMIC cake extract adsorption was reached in under 17 hours and was independent of the concentrations used.

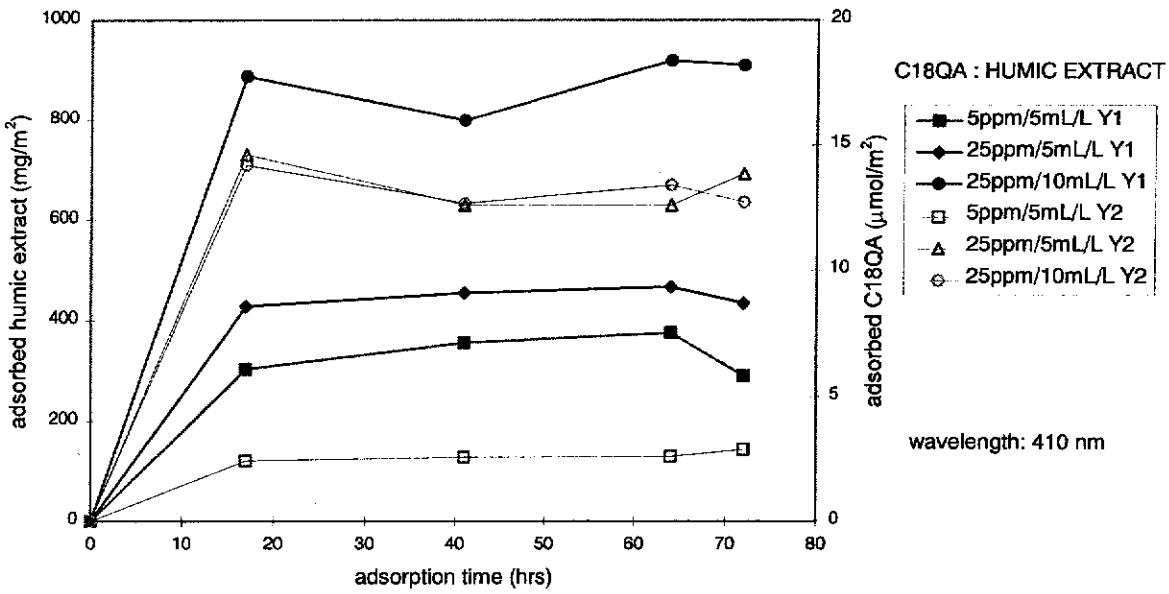

Figure 6.2: A plot of the adsorption of HUMIC cake extract (Y1, measured at 410 nm) and of C18QA (Y2) as a function of time at different C18QA and HUMIC concentrations

Results show that equilibrium was reached before 20 hours. Accordingly, for the adsorption measurements, 20 hours adsorption time was applied in every instance.

6.3.3 Adsorption of C18QA on glass from synthetic liquor

The glass surface is probably negatively charged in liquor, and may attract C18QA positive ions to adsorb. Adsorption of C18QA on the surface of the vessel

would decrease the concentration in solution. If this amount is significant, it should be taken account in the adsorption measurements.

The conditions used in the adsorption isotherm measurements were applied here without solid oxalate present. Figure 6.3 shows how much C18QA was adsorbed on the glass wall at different concentrations of C18QA.

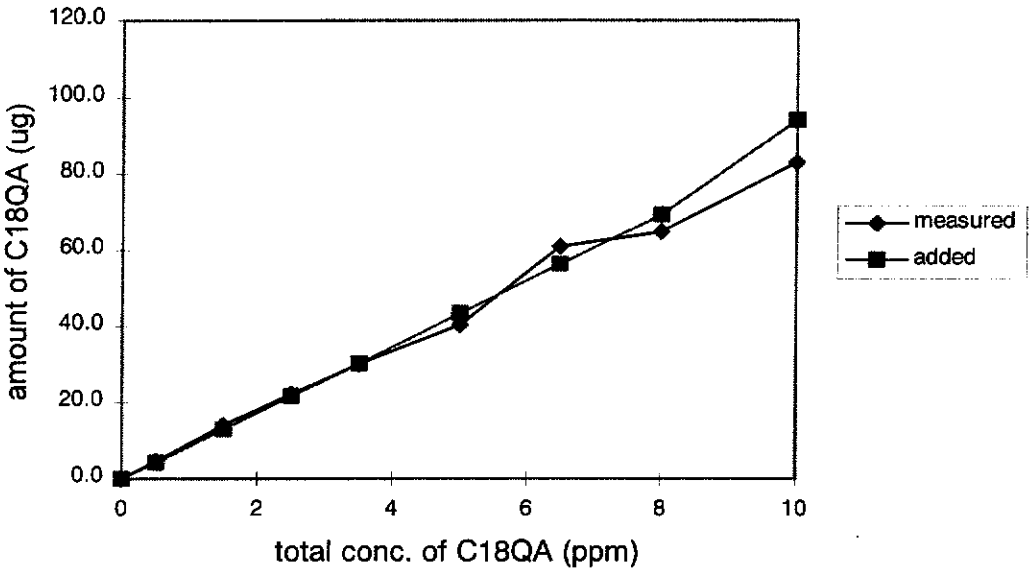

Figure 6.3: The amount of C18QA added and measured after adsorption on the glass surface of the container

No significant adsorption was measured under 5 ppm concentration of C18QA. Above 5 ppm, results showed that 5-10% of the C18QA was adsorbed. This is within the error of the analysis 10 RSD% and therefore was considered insignificant.

6.3.4 Precision and accuracy of the adsorption procedure developed

A method has been developed which can measure the amount of C18QA adsorbed on the oxalate surface and remaining in solution after adsorption. The typical precision of this procedure was found to be 25 RSD% for the C18QA, and the recovery was between 70-110% and 85-115% of the initial C18QA added for the C18QA and the C18QA/HUMIC cake extract mixture, respectively (Figure 6.4).

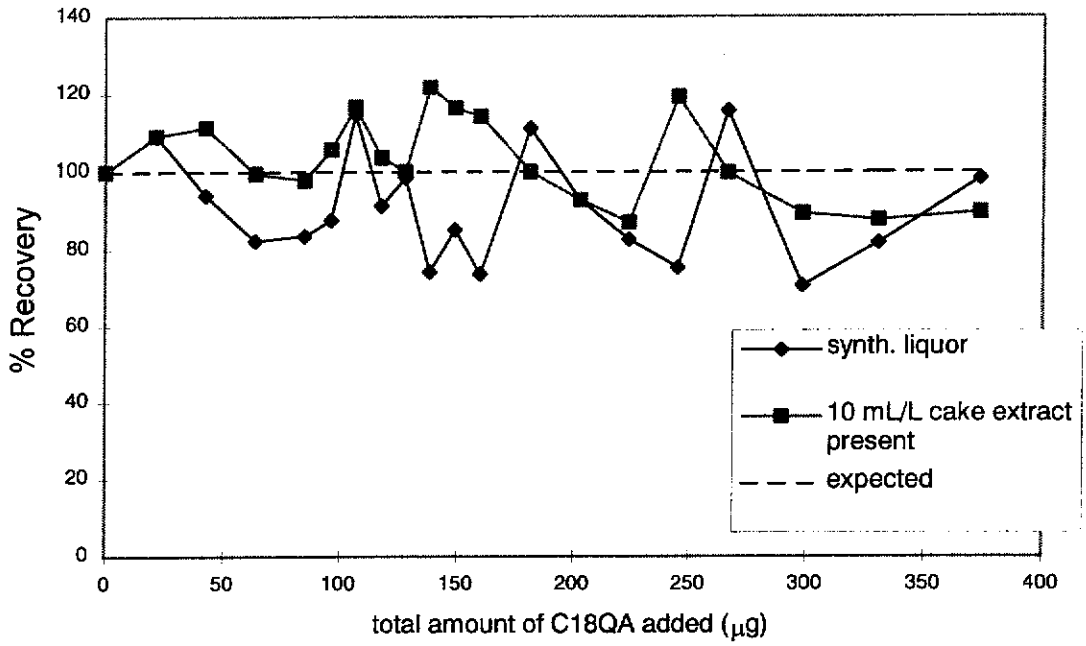

Figure 6.4: Recoveries of C18QA from the adsorption isotherm measurement in synthetic liquor with and without HUMIC cake extract.

6.3.5 Adsorption of C18QA on acicular oxalate from synthetic liquor

Based on crystallization test results in synthetic liquors, it was expected that C18QA would not show any adsorption on the surface of sodium oxalate, because it did not show any inhibitory effect on oxalate crystallization in pure synthetic liquor. However, an adsorption isotherm of C18QA in synthetic liquor was successfully generated on acicular sodium oxalate (Figure 6.5). The isotherm was found to conform to Langmuir type adsorption behaviour.

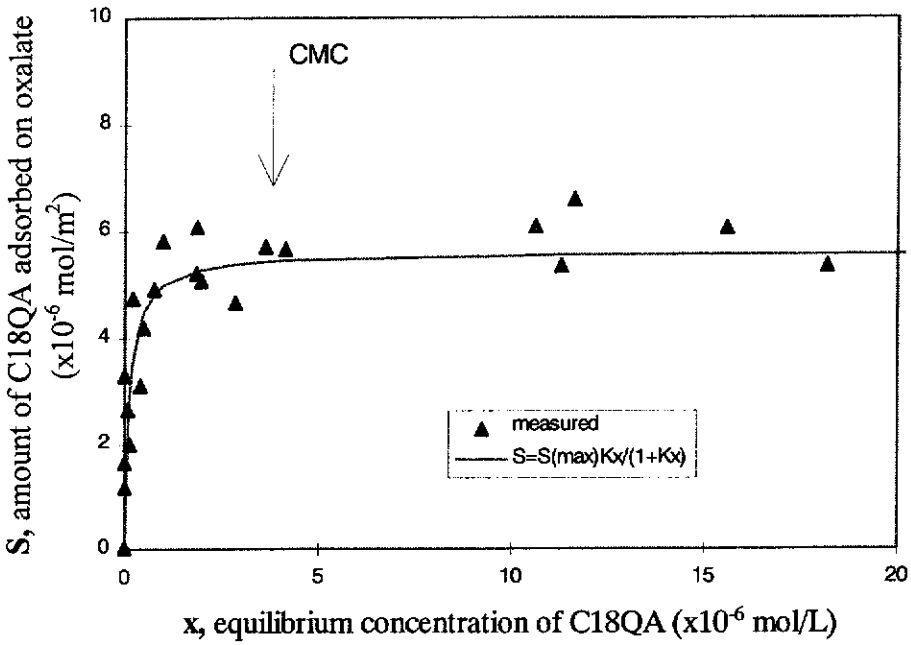

Figure 6.5: Adsorption isotherm of C18QA on acicular sodium oxalate measured in synthetic liquor in the presence of 5 g/L solid oxalate. The line represents the Langmuir function calculated with the parameters determined.

This behaviour indicates a high affinity of adsorbate towards the surface. The equilibrium constant or adsorption affinity (K) and the adsorption capacity ($S_{(max)}$) were obtained by plotting S^{-1} (the reciprocal surface concentration) versus x^{-1} (the reciprocal equilibrium concentration) of the C18QA.

K, adsorption affinity: 8.4 x 10^6 L/mol

$S_{(max)}$, adsorption capacity: 5.6 x 10^{-6} mol/m^2

Figure 6.5 shows that the Langmuir function calculated with the determined parameters correlates well with the experimental data. Calculated from the adsorption capacity, the area occupied by one molecule at the plateau region corresponds to ca 30 Å^2/molecule. This value is consistent with that found in the literature for similar compounds (Rubingh and Holland 1991) and suggests that molecules adsorb perpendicularly to the surface.

6.3.6 Effect of solid oxalate concentration on C18QA adsorption

In order to compare results for C18QA inhibition in MOSPIT tests it would be desirable to measure the isotherm using a 1.0 g/L solid oxalate concentration (the same as that used in the MOSPIT test). Moreover, the experimental conditions sometimes require changes in liquid/solid ratios in order to reach high solution concentrations, and the simplest way to do that is to change the solid concentration. Tests were therefore conducted to see what effect a change in solid oxalate concentration had on the adsorption isotherm.

Conventional adsorption isotherms are independent of the concentration of the solid loading due to the fact that they are normalised to a constant surface area. Contrary to this, the adsorption isotherm for C18QA was found to be dependent on the solid oxalate concentration (Figure 6.6).

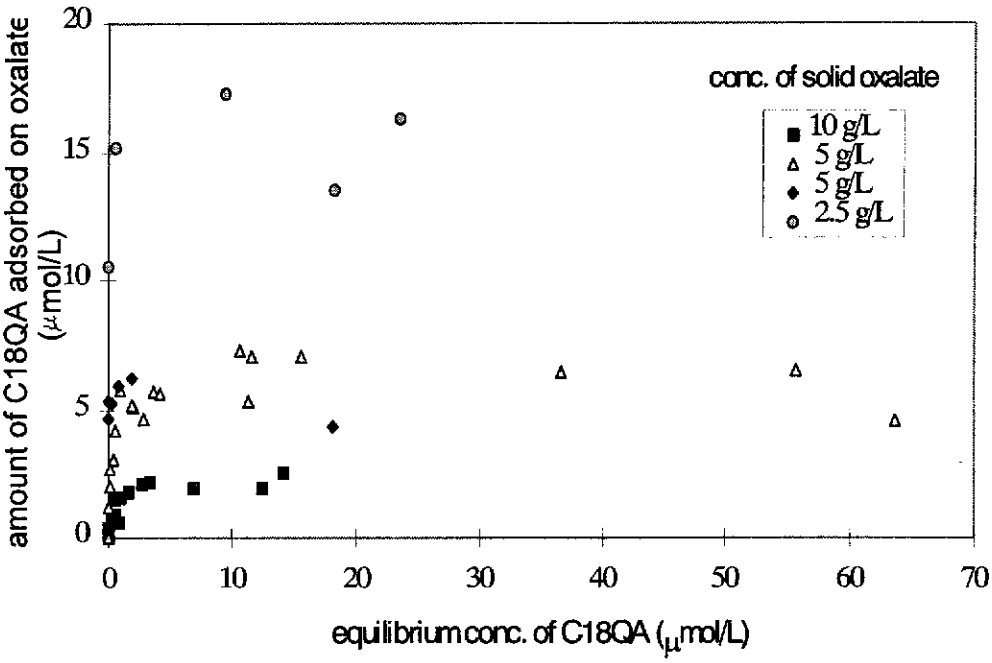

Figure 6.6: Adsorption of C18QA onto acicular sodium oxalate from synthetic liquor in the presence of different amounts of solid oxalate

The adsorption parameters, adsorption affinity (K), the adsorption capacity ($S_{(max)}$) and the area occupied by one molecule (A) were determined from the experimental data (as described above):

10 g/L solid concentration-

K_{10}, adsorption affinity: 1.6×10^6 dm^3/mol

$S_{(max)10}$, adsorption capacity: 2.4×10^{-6} mol/m^2

A_{10}, area occupied by one molecule: 65 $Å^2$/molecule

5 g/L solid concentration-

K_5, adsorption affinity: 8.4×10^6 dm^3/mol

$S_{(max)5}$, adsorption capacity: 5.6×10^{-6} mol/m^2

A_5, area occupied by one molecule: 30 $Å^2$/molecule

2.5 g/l solid concentration-

$K_{2.5}$, adsorption affinity: 4.0×10^7 dm^3/mol

$S_{(max)2.5}$, adsorption capacity: 1.6×10^{-5} mol/m^2

$A_{2.5}$, area occupied by one molecule: 10 $Å^2$/molecule

The amount of C18QA adsorbed onto a unit of the solid was much higher at low solid concentration. This behaviour implies one of two possibilities:

1. the solid oxalate may not have been well-dispersed in the synthetic liquor, or
2. the adsorption of C18QA may have occurred through a third participant present in liquor.

The first possibility means that at a high solid oxalate concentration there would be increased aggregation and thus less surface area available for adsorption. The second possibility means that another impurity in the liquor is required to co-adsorb with the C18QA. As the solid oxalate concentration increases the amount of impurity to adsorb per unit area decreases, this in turn leads to less C18QA adsorption per unit area.

The possibility of agglomeration of the solid oxalate particles, which would have reduced the available surface area, was investigated at various suspension concentrations by laser light scattering. The oxalate suspension was found to be well dispersed up to 50 g/L solid concentrations. Thus, agglomeration as an explanation of the observed behaviour was discounted.

Given that the liquors were purified with activated carbon prior to use, it was felt that the impurity that may be co-adsorbing with the C18QA would not be surface active organic in nature. It was postulated that a negatively charged metal complex may co-adsorb with the C18QA. Therefore, concentrations of metal

impurities in the synthetic liquor were determined before and after the adsorption procedure, with and without C18QA present. Calcium adsorption onto the solid oxalate was found. However, measurement of the C18QA adsorption in the presence of different calcium concentrations in solution did not indicate any difference, and thus, the idea of metal-C18QA co-adsorption was discounted.

We could not find the minor component responsible for the C18QA adsorption isotherm being solid concentration dependent. It seemed from these preliminary investigations that to identify this impurity would take much time away from the research without contributing to solving the original problem. Therefore, these investigations were terminated.

6.3.7 Effect of pH and ionic strength on C18QA adsorption

The synthetic liquor contains many different components. To clarify which liquor characteristic or component may affect the adsorption of C18QA, solutions of different compositions were made up, and the adsorption of C18QA onto acicular oxalate was determined in these solutions. It was thought that finding a less complex system than the synthetic liquor in which C18QA adsorption was measured would help to understand how this surfactant adsorbs on oxalate from liquor.

The following solutions were made up and saturated with sodium oxalate:

I. 5 M NaCl
II. 1 M NaOH & 4 M NaCl
III. 3.5 M NaOH & 1.5 M NaCl
IV. Water ($Na_2C_2O_4$ = 0.3 M)
V. Synthetic liquor without the organic anions: formate, acetate, malonate, succinate. Ionic strength matched by using NaCl ($[Na^+]$=6.87 M)
VI. Synthetic liquor ($[Na^+]$=6.87 M)

The adsorption of C18QA was determined in these solutions and the experiments were repeated in solutions that had been purified with activated carbon. The initial concentrations of C18QA were 10 and 30 ppm and the solid oxalate concentration was 5 g/L. After an overnight equilibration, the solid phase was separated and the amount of C18QA adsorbed was determined. Duplicate experiments were

undertaken. Figure 6.7 shows the amount of C18QA adsorbed on oxalate in the various solutions.

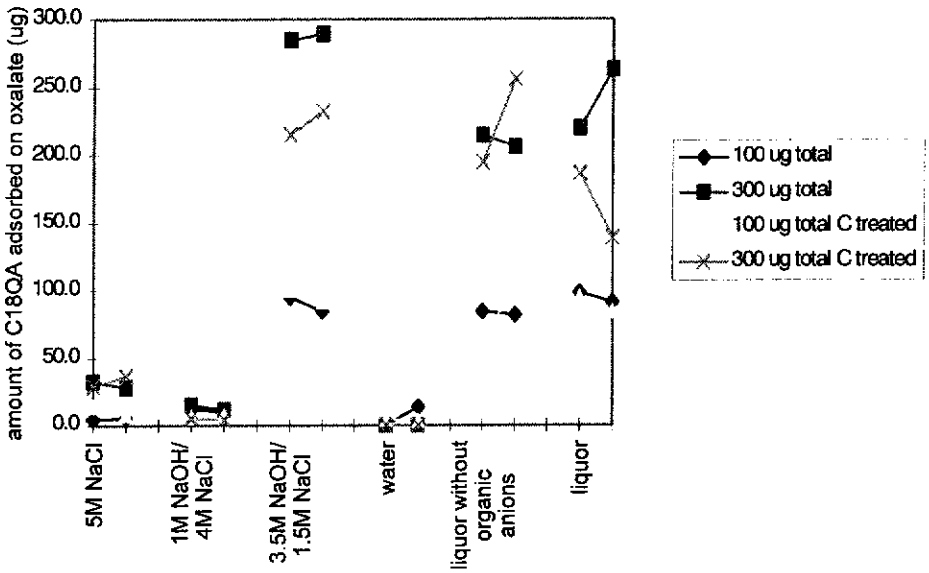

Figure 6.7: The amount of C18QA adsorbed on acicular sodium oxalate from solutions of different pH and ionic strength

No adsorption was measured from water, 5 M NaCl or 1M NaOH/4 M NaCl solutions. Significant adsorption was found from 3.5 M NaOH/4 M NaCl, synthetic liquor without the organic anions or from standard synthetic liquor. These results indicate that the pH of the solution plays an important role in dictating the chemistry of the adsorption. The increase in NaOH concentration from 1M to 3.5M resulted in significant adsorption of C18QA on oxalate. Removing the organic anions known from the liquor, while maintaining the same ionic strength and NaOH content, did not affect the adsorption. This behaviour may imply that the third participant necessary for the adsorption is an unknown organic compound, and its active form depends on the pH of solution, ie deprotonation or complexation.

6.3.8 Adsorption of HUMIC cake extract on acicular oxalate from synthetic liquor

Plant humates, HUMIC plant extract and HUMIC cake extract, were shown to have an impact on oxalate yield without the presence of QAs (section 3.3.1). Thus, it was expected that significant adsorption of plant humates would occur on the oxalate surface.

The adsorption isotherm of the HUMIC cake extract was successfully determined on acicular oxalate. Figure 6.8 shows the adsorption isotherm for the HUMIC cake extract determined by UV-VIS spectrophotometry at different wavelengths. The arrow indicates 2.25 g/L, the CMC of the HUMIC cake extract (McKinnon, Shaw, Sipos, Smith & Xu, 1998).

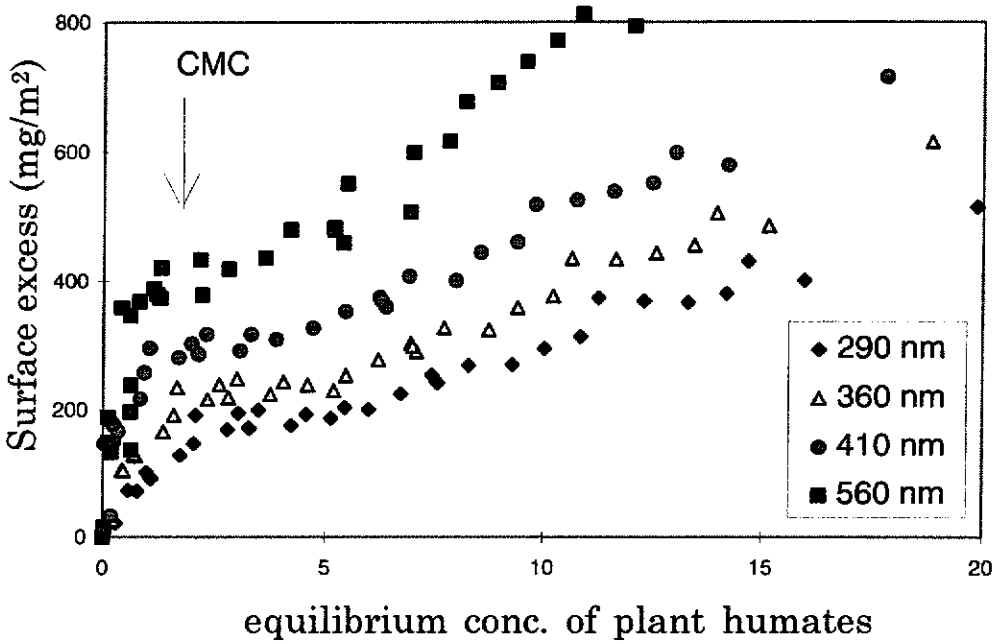

Figure 6.8: Adsorption isotherm of HUMIC cake extract on acicular sodium oxalate in synthetic liquor measured at different wavelengths

The adsorption isotherm of HUMIC cake extract shows a continuous increase of HUMIC adsorbed on the oxalate surface. Different extents of adsorption were detected at different wavelengths. The higher the wavelength, the higher the level of the adsorbed amount of HUMIC cake extract. Plant humates are mixtures of compounds, and some of the components probably adsorb preferentially onto the oxalate surface. Size and degree of functionalities dictate the absorbance of humates. It is assumed that the adsorption measured at higher wavelengths represents the behaviour of the higher molecular weight components of the mixture. This would explain why different extents of adsorption are measured at different wavelengths.

In the adsorption isotherms, a "knee" in the curve was observed close to the measured CMC for HUMIC cake extract in synthetic liquor. This indicates that

adsorption above this value probably consists of micelles of humates rather than single species adsorption.

6.3.9 Adsorption from mixture of C18QA and HUMIC cake extract

Both HUMIC cake extract and C18QA have been shown to adsorb individually onto sodium oxalate from synthetic liquor. However, the inhibitory effect of C18QA on oxalate crystallization was observed only when both HUMIC material and C18QA were present together. The simultaneous adsorption of both C18QA and HUMIC cake extract from the same solution was measured (constant HUMIC cake extract concentration 10 mL/L, varying C18QA concentrations).

It was found that these materials enhanced the adsorption of each other. Figure 6.9 shows the amount of HUMIC cake extract adsorbed on the solid oxalate as a function of the amount of C18QA adsorbed onto the same oxalate surface. The dotted line indicates the adsorption capacity for C18QA measured in the absence of HUMIC cake extract.

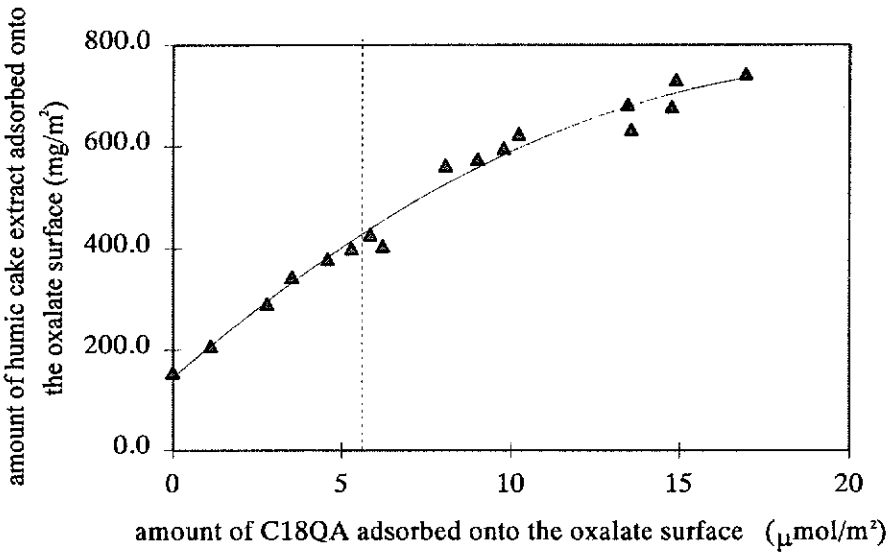

Figure 6.9: A plot of the amount of HUMIC cake extract adsorbed on acicular sodium oxalate (measured at 290 nm) as a function of the amount of C18QA adsorbed onto the same oxalate surface at the same time in synthetic liquor.

The C18QA adsorption isotherm showed that a plateau occurred at 5.6 μmol/m^2 (section 6.3.5). Figure 6.9 shows that significantly more than 5.6 μmol/m^2 can be adsorbed when the HUMIC cake extract is present. Similarly,

the amount of plant humates adsorbed is significantly greater (5x) in the presence of C18QA. This suggests a mechanism of co-adsorption, whereby the C18QA and humates interact together at the oxalate surface. It is possible that this interaction is an electrostatic one (section 6.3.10). The overall result is a more hydrophobic (surface active) molecule which has a greater propensity to adsorb and block growing sites on the oxalate crystal.

The enhanced adsorption of HUMIC cake extract in the presence of C18QA may be the clue to the stabilizing effect of QAs measured in plant liquors. Quaternary amines probably do not play an active role in the stabilization of sodium oxalate by poisoning the oxalate crystals, because they were shown to have no effect on oxalate crystallization without plant organics present in synthetic liquor. Rather, their action is to interact with plant organics and to attract excess organics to adsorb on the oxalate surface.

6.3.10 Interaction between C18QA and HUMIC cake extract

We were interested in determining whether the C18QA-HUMIC interaction occurs in solution prior to adsorption. Experiments were conducted whereby C18QA was added at various doses (0, 10, 20, 30, 50, 100 or 200 ppm) to synthetic liquor containing HUMIC cake extract (10 mL/L). No solid sodium oxalate was present. The resultant solutions were then observed over a 24 hours period. A black precipitate was evident from liquors containing 30 ppm or higher concentrations of C18QA after 24 hours, and the amount of this precipitate increased with increasing C18QA dosage.

From this observation it was concluded that the effect of C18QA on oxalate crystallization in the presence of HUMIC cake extract was to precipitate humic material from solution onto the oxalate surface. This mechanism of QA-HUMIC precipitation has been previously observed for materials such as PolyDADMAC (Roe and Malito 1986). It is generally accepted that the positively charged QA ions are attracted to the negatively charged humates, thus neutralizing the charge and making the humic precipitate out of solution (Lever 1981).

6.3.11 Adsorption of C18QA on acicular sodium oxalate in plant liquor

An attempt has been made to measure the adsorption isotherm of C18QA in plant liquor using the method developed. However, it was found that sodium

oxalate precipitated out from plant liquors during the adsorption period. The original oxalate concentration dropped from 2.14 g/L to 1.81 g/L (6% of the solid oxalate already present as solid phase). Therefore, it was postulated that the method developed for adsorption measurements in synthetic liquor was not suitable for similar measurements conducted in plant liquor. The preparation of liquors with low oxalate concentrations was not developed at the time of this study. Even the solubility of sodium oxalate in plant liquor was still a question.

6.3.12 Role of the excess HUMIC adsorbed in the inhibition of oxalate crystal growth

The question arises as to whether the enhanced crystal growth inhibition measured from liquors containing both the HUMIC cake extract and the C18QA, is due simply to the excess humates adsorbed on the oxalate surface, ie whether the adsorbed C18QA plays an active role in this inhibition or simply modifies the impact of the HUMIC cake extract on oxalate crystallization. To clarify this, the MOSPIT results from solutions of the HUMIC cake extract with or without the presence of C18QA or N138# were measured, and systems which resulted in the same oxalate yield were compared, whether the amounts of the adsorbed HUMIC were equal or not.

Humic cake extract solutions of 0, 2, 4, 6, 8 and 10 mL/L were made up in synthetic liquor, and either 5 or 10 ppm of C18QA or N138# was dosed into the liquor solutions. Their impact on the oxalate yield was measured with the MOSPIT test (section 2.2.4). The concentrations of the HUMIC cake extract depleted from solutions (adsorbed on solid oxalate) during crystallisation were determined (section 3.2.2). Figure 6.10 shows the increase in adsorbed HUMIC cake extract (calculated from the decrease in absorbance of the HUMIC cake extract in liquor) with increasing QA concentrations in the system. Figure 6.11 shows the oxalate yields that resulted from the same solutions.

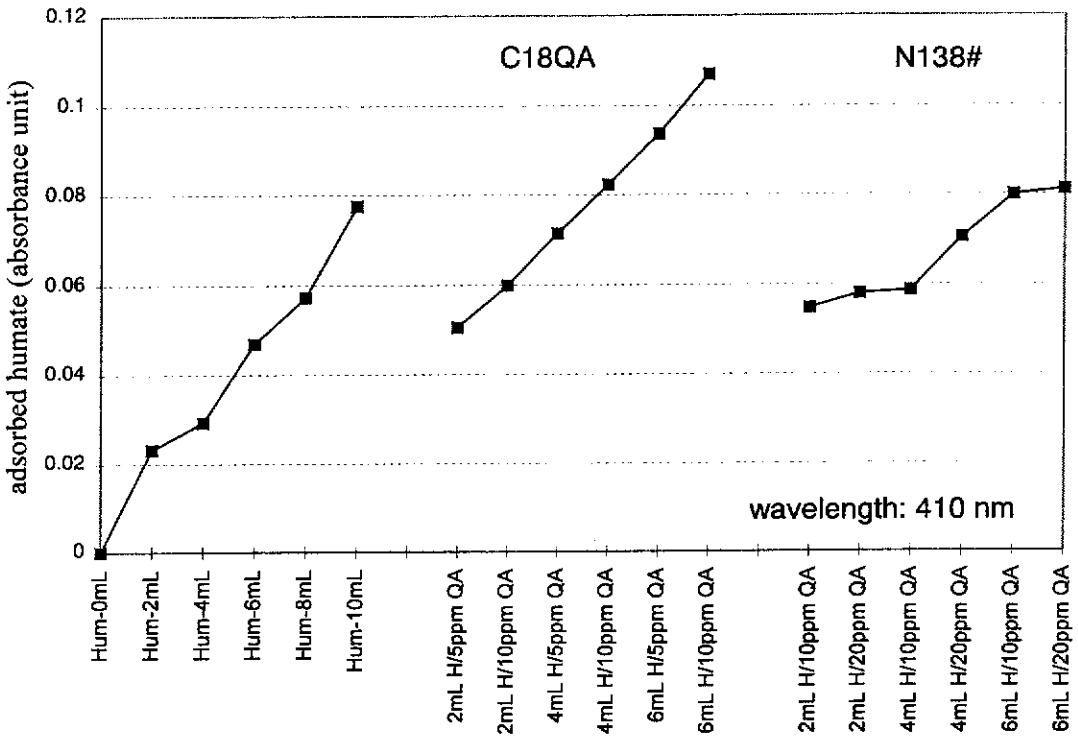

Figure 6.10: The decrease in the concentration of the HUMIC cake extract (Hum or H) in solution due to the adsorption on acicular oxalate in systems containing C18QA or N138# at different concentrations. Absorbances were measured at 410 nm.

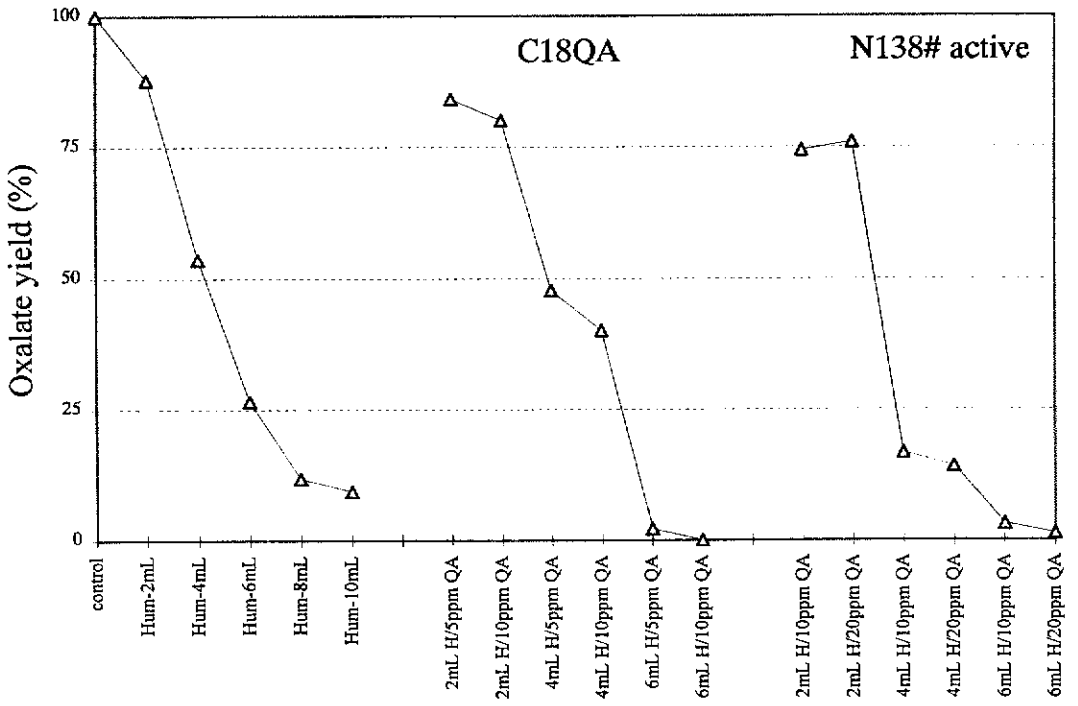

Figure 6.11: MOSPIT results of the HUMIC cake extract with or without the presence of C18QA or N138#.

The presence of QAs in solution increased the amount of HUMIC cake extract adsorbed, which resulted in an increased level of growth inhibition and a lower oxalate yield. If the amount of HUMIC cake extract adsorbed from a particular solution (Figure 6.10) is compared with the corresponding oxalate yield (Figure 6.11), it is seen that solutions containing QAs did not result in the amount of growth inhibition expected on the basis of the amount of HUMIC cake extract adsorbed. For example, solutions containing the following additions:

the 8 mL/L humic extract,

the 2 mL/L humic extract + 10 ppm C18QA and

the 2mL/L humic extract + 20 ppm N138#

all had the same amount of adsorbed humate (Figure 6.10). However, 8 mL/L humic extract solution resulted in a much lower yield than the solutions containing QAs (Figure 6.11). This implies that the excess HUMIC cake extract did not adsorb in the same way or occupied less active sites, resulting in a less efficient inhibition of oxalate crystal growth. This observation will be confirmed with the results measured with the confocal laser microscope (section 7.3).

The QAs do not seem to play an active role in the inhibition of oxalate crystal growth. In the presence of the HUMIC cake extract, they make it suitable for more humates, 2-3 times more, to adsorb. This role is probably due to the opposite electrostatic charge of these QAs and the humates. If the QAs have adsorbed onto sites on the oxalate crystals that do not block crystal growth, subsequent co-adsorption of humates onto them may similarly be ineffective in modifying growth. However, the QAs may also increase the amount of humates adsorbed onto sites that block crystal growth, resulting in the enhanced inhibition of crystal growth.

6.4 Conclusions and Recommendations

6.4.1 Conclusions

As we had a method established for its analysis, the adsorption behaviour of the strongest crystal growth inhibitor, C18QA was investigated with or without the presence of the HUMIC cake extract.

An adsorption procedure was developed for C18QA and for the HUMIC cake extract. The sufficient adsorption time to reach equilibrium from a mixture of C18QA and the HUMIC cake extract was established and set to 20 hours. The chemical stability of the HUMIC cake extract for the adsorption period was

checked and found to be satisfactory. No significant adsorption of C18QA was measured on the glass surface of the container. The precision of the adsorption measurement from a solution of the individual components or from a mixture of C18QA and the HUMIC cake extract was found to be 25 RSD% and the recovery was 70-115%.

Contrary to the fact that QAs did not inhibit crystal growth of sodium oxalate in synthetic liquor, an adsorption isotherm of C18QA was successfully generated on acicular sodium oxalate. The adsorption isotherm conformed to Langmuir-type adsorption behaviour with 8.4×10^6 L/mol adsorption affinity and 5.6×10^{-6} mol/m^2 adsorption capacity. However, the adsorption isotherm was found to be dependent on the solid oxalate concentration. Investigations were undertaken to clarify the reason of this unusual dependence on the solid content. These investigations covered the possibility of insufficient dispersion of solid oxalate and of pre-adsorption of a third participant that promoted the adsorption of C18QA. However, the solid oxalate was found to be well dispersed in liquor. Although calcium adsorption onto oxalate had previously been found, no difference in adsorption of C18QA was measured at different Ca concentrations. The minor component responsible for the C18QA adsorption isotherm being dependent on solid concentrations could not be found. Adsorption measurements of C18QA in different solutions, however, revealed that an extremely high pH was essential for this third participant, presumably an organic compound, to interact.

Plant humates were shown to be good crystal growth inhibitors of sodium oxalate. Accordingly, adsorption of the HUMIC cake extract on solid oxalate was expected and measured successfully. The adsorption isotherm shows a continuous increase of humic substances on the oxalate surface with increasing humic concentration in liquor. The adsorption of higher molecular weight components of the mixture of organics in the HUMIC cake extract, measured at high wavelengths, was more extensive.

The simultaneous adsorption of both C18QA and HUMIC cake extract was measured from a mixture of these components. It was found that these components enhanced the adsorption of each other. Significantly more C18QA and humates were adsorbed on the solid oxalate from a mixture than from equivalent solutions of the individual components. This co-adsorption was probably the result of an electrostatic interaction between the positively charged C18QA and the negatively

charged humic material on the surface of solid oxalate. Further investigations revealed that this interaction existed between QAs and HUMIC cake extract in liquor solutions at high concentrations of the components. It was concluded that the effect of C18QA on oxalate crystallization in the presence of HUMIC cake extract was to precipitate humic material from solution onto the oxalate surface. This was possible at a much lower concentration of components when solid oxalate was present, for the adsorption concentrated the participants on the surface of oxalate, therefore the solubility product could be reached locally.

A question arose whether the adsorbed C18QA played an active role in the inhibition of oxalate crystal growth or simply modified the impact of the HUMIC cake extract on oxalate crystallization. We compared the amount of HUMIC cake extract adsorbed from solution with the corresponding oxalate yield. It was seen that solutions containing QAs resulted in less enhancement of growth inhibition than was expected on the basis of the amount of HUMIC cake extract adsorbed. This implied that the excess HUMIC cake extract did not adsorb in the same way as the humates without QA, or, alternatively, occupied less active growing sites, resulting in a less efficient inhibition of oxalate crystal growth.

6.4.2 Recommendations

The mechanism of the adsorption of C18QA and of the HUMIC material on acicular sodium oxalate in synthetic liquor is not clear. Charged surfaces usually favour the adsorption of a species of opposite charge. Due to the very high ionic strength of liquor, the surface of sodium oxalate is presumably charged. It is still a question how both positively and negatively charged molecules can adsorb on the same surface.

There are some attempts to develop a technique for surface charge measurements in liquors using ultrasound. With the knowledge of the surface charge, the possible mechanism of adsorption will be more predictable.

Besides C18QA, only N138# co-adsorption with the HUMIC cake extract was measured. The behaviour of this surfactant was very similar to that of C18QA. It would be interesting to compare all of the QAs regarding their adsorption characteristics and the amount of humates adsorbed together with the QAs onto the oxalate surface.

Chapter 7

Confocal Imaging of Humic Cake Extract Adsorbed on Acicular Oxalate or Incorporated in the Oxalate Crystals

7.1 Introduction

Confocal Laser Scanning Microscopy (CLSM) is commonly used to image biological samples, in which either naturally occurring or added fluorescent molecules (dyes) are excited by the powerful monochromatic laser light, and the emitted fluorescence light is detected. Applying this technique to our samples gives us the possibility to track the humates adsorbed on the surface of acicular sodium oxalate or incorporated in oxalate crystals produced from solutions containing humic material. The digital imaging capability and very narrow depth of focus of CLSM allow the distribution of the humates to be seen inside the crystals by mapping layers at a 10 μm depth.

7.2 Experimental

7.2.1 Sample preparation

Crystals with HUMIC adsorbed: Clean acicular oxalate crystals (2-3 mm) were produced from synthetic liquor, filtered and washed with 50%, 90% and 100% ethanol/water solutions that were saturated with sodium oxalate prior to use. Blocky oxalate crystals were produced from water, filtered and washed with 50%, 90% and 100% ethanol/water solutions as well. In a few instances, ie Figure 7.2, the original seed (section 2.2.1) was applied. These crystals were used for the adsorption investigations. The crystals were conditioned in synthetic liquor dosed with 20 mL/L HUMIC cake extract overnight. The crystals were filtered without washing, and the humic material adsorbed on the surface imaged with CLSM. Experiments were repeated in the presence of 30 ppm of C18QA. Control images were obtained with

crystals treated with a solution of 30 ppm of C18QA without any HUMIC cake extract present

Crystals with HUMIC incorporated: Synthetic liquor was saturated with sodium oxalate at 80 °C, purified with activated carbon and filtered. The liquor was dosed with 10 mL/L HUMIC cake extract with or without 20 ppm of C18QA present, and left at room temperature. After 2 days, the crystals precipitated were filtered and washed with 50%, 90% and 100% ethanol/water solutions.

7.2.2 Imaging

Crystals were examined using a Bio-Rad MRC-1000 confocal laser scanning microscope (CLSM). The CLSM was equipped with a Krypton - Argon laser. Images were collected using the 488 nm line of the laser and a 515 nm barrier emission filter. Either a 4x lens (plan apo, Nikon) with a numerical aperture (NA) of 0.25 or a 20x lens with a NA of 0.75 was used. The pixel sizes were 3.9 μm^2 for the 4x lens and 0.8 μm^2 for the 20x lens. The black level was adjusted to give a dark current signal of 2 - 5 pixel intensity. The gain was set to give the full dynamical range (max. 255 pixel intensity) for all images. Optical sections (Z-series) were collected with a stepping size of 10 µm for the 4x lens and 2 µm for the 20x lens. Z-series were projected using the software "Confocal Assistant" (by T. Breijle). The maximum algorithm was employed resulting in extended focus images.

7.3 Results and Discussions

7.3.1 HUMIC cake extract adsorbed on the sodium oxalate surface

Figure 7.1 shows that the acicular oxalate with C18QA adsorbed on the oxalate surface does not give a signal under the confocal microscope. Under the microscope, humic material emits fluorescent light, therefore, the HUMIC cake extract can be detected. Neither the sodium oxalate, nor the C18QA give any signal.

Figure 7.1: Control image. Confocal image of C18QA adsorbed on acicular oxalate. No signal is detected.

Figure 7.2 shows the adsorbed HUMIC cake extract on the surface of acicular sodium oxalate. In this experiment, the original oxalate seed (section 2.2.1) was conditioned in humic solution with or without the presence of C18QA. Images were taken with the same instrument set up, laser intensity and detection time. The brighter image of Figure 7.2b in the presence of C18QA indicates an enhanced adsorption of humates on the surface. These results confirm that more humic material adsorbed on sodium oxalate from a mixture of C18QA and HUMIC cake extract. These results are consistent with the ones obtained from direct adsorption measurements (section 6.3.9).

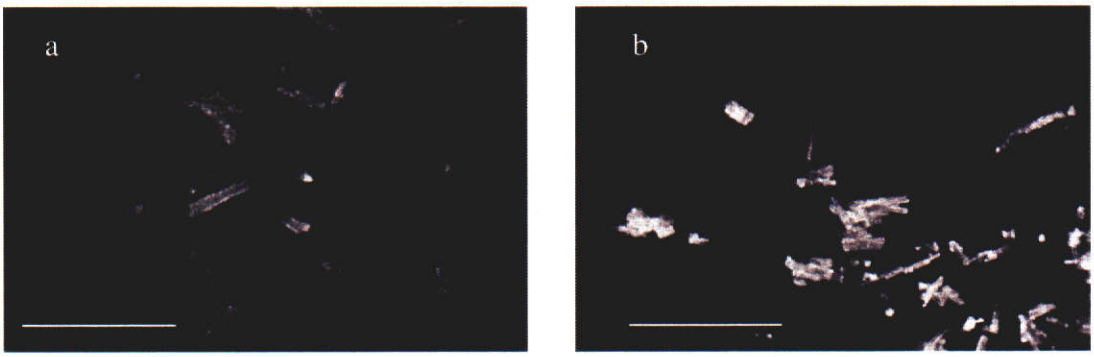

Figure 7.2: Confocal images of HUMIC cake extract adsorbed on acicular oxalate from a) HUMIC cake extract solution b) HUMIC cake extract and C18QA solution. The scale bar represents 250 μm.

Bigger crystals were produced and the magnification was increased in order to observe the adsorption of humates on the surface of oxalate crystals. Figure 7.3 shows that the adsorption of humates occurred all around the crystal including the

end faces. Patches of plant humates can be recognized on the surface, showing that the adsorption is not even. The images indicate that the humic material preferably adsorbed in the corners and on the edges of the crystals.

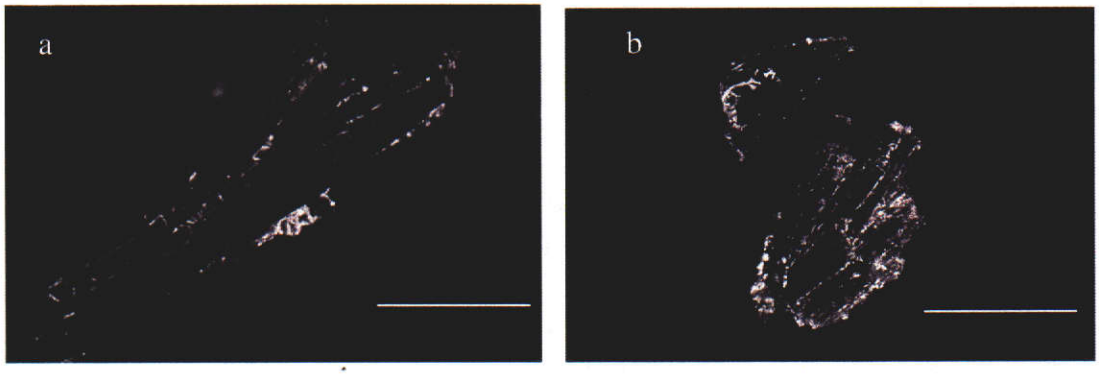

Figure 7.3: Confocal images of HUMIC cake extract adsorbed on acicular oxalate. No C18QA is present. The scale bar represents 1000 μm.

Images of Figure 7.4 were taken after having conditioned the crystals in a mixture of HUMIC cake extract and C18QA.

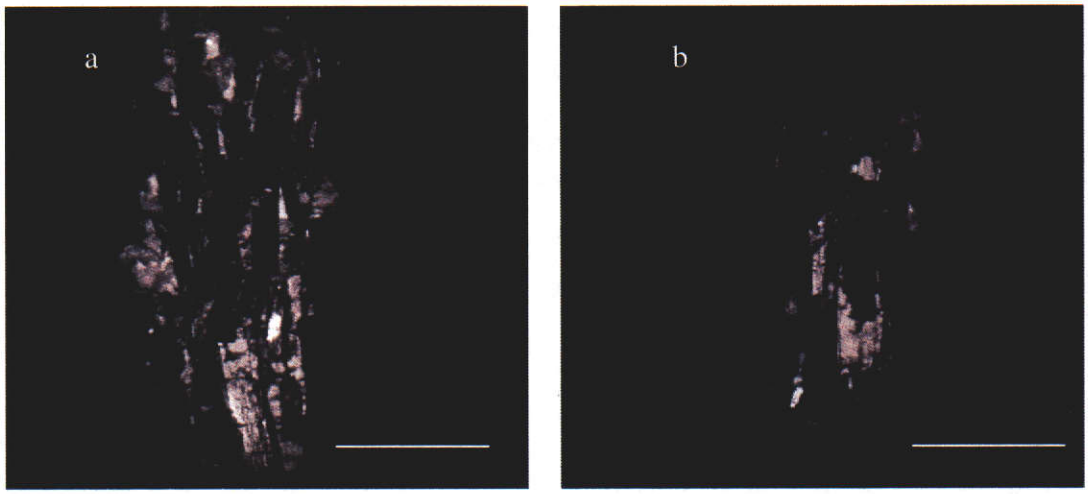

Figure 7.4: Confocal images of HUMIC cake extract adsorbed on acicular oxalate in the presence of C18QA. The scale bar represents 1000 μm.

The adsorption of humates, in the presence of C18QA, occured not only at the edges of the crystals, but on the side faces as well. A continuous layer of adsorbed humates can be seen on the major crystal faces. This can explain why the excess HUMIC cake extract adsorbed as the results of the QAs present was not as effective an inhibitor as the HUMIC cake extract on its own (section 6.3.12). The excess

HUMIC did not occupy the fast growing end faces; much HUMIC was adsorbed on the faces that did not contribute significantly to the overall growth.

Figure 7.5 shows the adsorbed plant humates on the surface of blocky sodium oxalate. Patches on the surface can be recognised. No difference in the presence of C18QA can be seen.

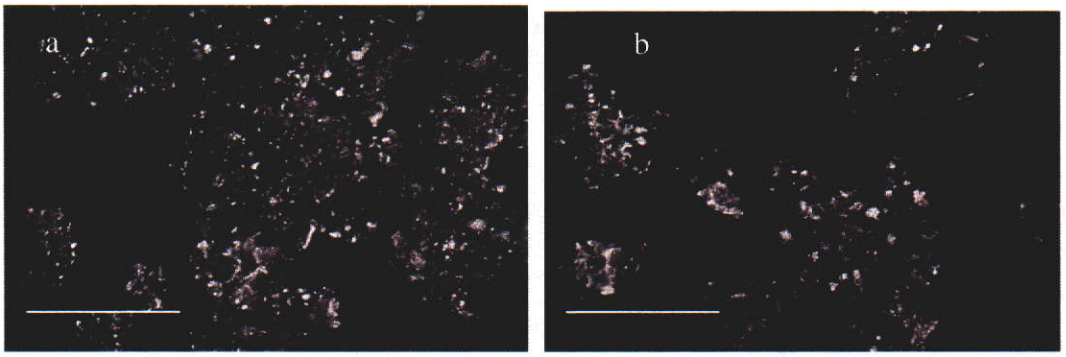

Figure 7.5: Confocal images of HUMIC cake extract adsorbed on blocky oxalate from a) HUMIC cake extract solution b) HUMIC cake extract and C18QA solution. The scale bar represents 250 μm.

7.3.2 HUMIC cake extract incorporated in the sodium oxalate crystals

With nucleation, the needle-like acicular sodium oxalate is produced under plant conditions. However, from synthetic liquor containing only HUMIC cake extract, sodium oxalate precipitates out in a ball-like morphology under conditions of very low supersaturation and at room temperature (Figure 7.6a). The confocal images clearly present that the humic material is incorporated inside the oxalate crystal. Mapping the layers, the humates show a very even distribution inside the oxalate crystals (Figure 7.6b).

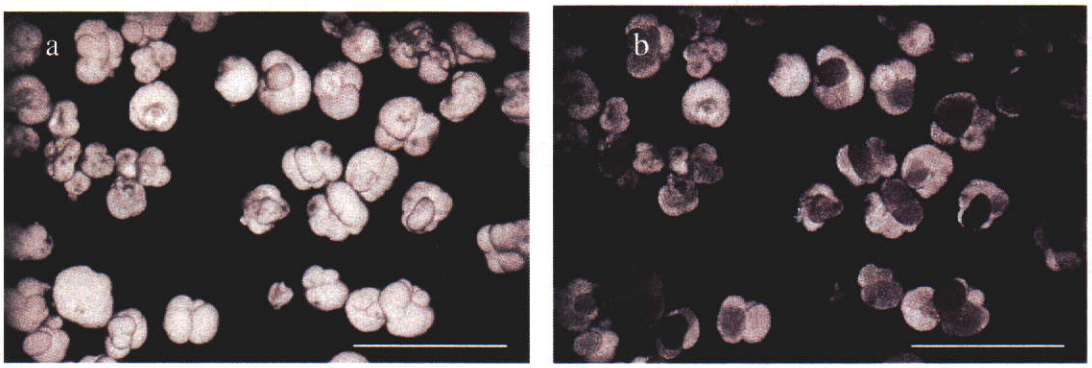

Figure 7.6: Confocal images of HUMIC cake extract incorporated in sodium oxalate crystals precipitated from humic liquor solution a) 32 Z-series projected b) image of one layer (20th) at 200 μm depth. The scale bar represents 1000 μm.

Figure 7.7 shows that the ball-like oxalate crystals become doughnut-like in the presence of C18QA. Optical microscope examinations confirmed that the holes appearing in the centre of the crystals were really the results of discontinuity of sodium oxalate and not only the discontinuity of humates.

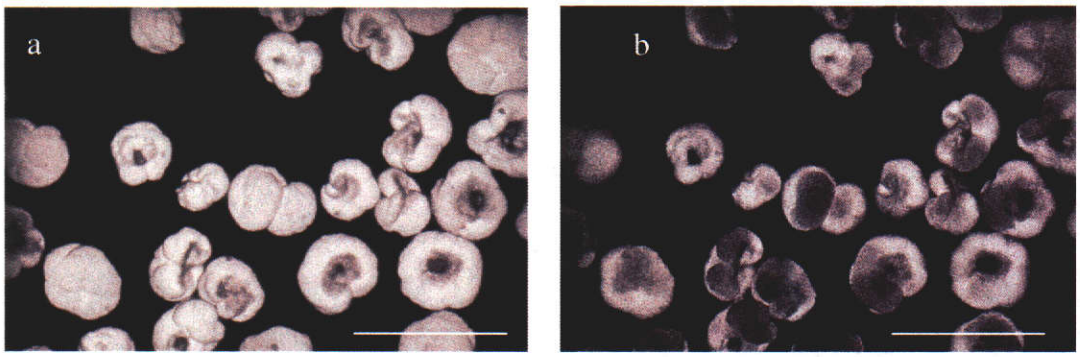

Figure 7.7: Confocal images of HUMIC cake extract incorporated in sodium oxalate crystals precipitated from HUMIC cake extract and C18QA liquor solution a) 39 Z-series projected b) image of one layer (20th) at 200 μm depth. The scale bar represents 1000 μm.

7.4 Conclusions and Recommendations

7.4.1 Conclusions

A technique, that is commonly used for imaging biological samples after treating the tissues with dyes, was employed to image plant humic material adsorbed

on solid oxalate crystals. Humic material is a naturally fluorescent substance. Neither sodium oxalate nor C18QA fluoresces under the confocal microscope.

Solid acicular oxalate was conditioned in liquor containing HUMIC cake extract. The HUMIC cake extract adsorbed all over the surface of the oxalate crystals including the end faces that were the main growing faces. The humic material preferentially occupied the edges and corners of the crystals. The adsorption was not even, patches of humic material formed on the surface.

The intensity of fluorescence increased after conditioning of the crystals in a mixture of HUMIC cake extract and C18QA. This indicated that significantly more humic material adsorbed on the crystal surface from the mixture. This result was consistent with the ones obtained with direct adsorption measurements.

In the presence of C18QA, humic material adsorbed on the main crystal faces as well as at the edges and in the corners. The growth rate of the main faces is slow. This rate does not contribute much to the overall growth rate. That can explain why the excess humic material adsorbed with C18QA was less effective as an inhibitor than would have been expected from the amount of humic material adsorbed. The excess humic material did not adsorb on the fast growing faces; some of it occupied crystal faces that did not contribute much to the overall growth rate.

Humic material of cake extract adsorbed on blocky sodium oxalate as well. Unfortunately, there are no crystallization results to compare the quantitative data to the images. No obvious difference was seen in the presence of C18QA.

The nucleation of oxalate from HUMIC cake extract liquor solution resulted in crystals with a different morphology. Ball-like crystals, "poppy seed" crystals were formed. It could be observed with the confocal microscope that the humic material was incorporated in the crystal lattice.

From a mixture of C18QA and HUMIC cake extract, doughnut-like crystals with a hole in the middle of the crystals were formed.

7.4.2 Recommendations

Humic material adsorbed on blocky oxalate showed a pattern different from the one seen on acicular oxalate. The presence of C18QA did not cause visible change in the adsorption of humic material. It would be interesting to measure the effect of QAs and humates on the oxalate crystallization in the presence of blocky

oxalate. The adsorption procedure developed for acicular oxalate would be also suitable for blocky oxalate without alteration.

The formation of "poppy seed" oxalate occurs under plant conditions. However, the exact conditions are not known, and very little is known of the crystal structure of this humate-sodium oxalate crystal form.

Chapter 8

Fourier Transform Infrared Attenuated Total Reflection Spectroscopic Measurements of C18QA Adsorbed on Sodium Oxalate

8.1 Introduction

FTIR is a powerful technique for identifying inorganic and organic molecules that absorb infrared radiation. Vibrational absorption by molecules occurs in the infrared region, where the energy of radiation is insufficient to excite electronic transitions. Variations of rotational levels give rise to a series of peaks for each vibrational state.

Quaternary amines have infrared spectra (Kung and Hayes 1993; Weers and Scheuing 1991). Their characteristic bands appear around 2925 and 2855 cm^{-1} due to asymmetric and symmetric CH_2 stretching vibrations of the methylene group respectively, and around 2955 and 2875 cm^{-1} assigned to the R-CH_3 asymmetric and symmetric stretching vibrations, respectively. No other bands were obtained from their aqueous solutions.

FTIR spectroscopy has the ability to characterise the surfaces of solids. Techniques such as transmission FTIR and diffuse reflectance (DRIFT) spectroscopy have been widely utilised in the study of solid surfaces. Importantly, FTIR spectroscopy also has potential for the examination of solid surfaces in solution. Attenuated Total Reflection (ATR) FTIR provides a means of producing infrared spectra from *in situ* investigations of the solid/aqueous interface (Harrick 1967). ATR is a type of internal reflection spectroscopy (IRS) in which the sample is placed in contact with an internal reflection element (IRE) of high refractive index. Infrared radiation is focussed onto the edge of the IRE, reflected through the IRE, and then directed to a suitable detector. Although complete internal reflection occurs at the sample/IRE interface, radiation penetrates a short distance into the sample, where it can be absorbed. An absorption spectrum of the sample in contact with the IRE can

thus be obtained (Harrick 1967). Thus, ATR provides a viable means of investigating the solid/aqueous interface directly. Additionally, the very reproducible pathlength obtainable with ATR permits the accurate subtraction of water absorption peaks, and facilitates the investigation of aqueous systems.

The adsorption of C12QA, C14QA and C16QA on sodium oxalate has already been investigated by FTIR-ATR (Hind *et al*, 1997). Adsorption of QA was not found from solution of 4 M NaCl / 1 M NaOH solution. However, adsorption from a mixture of QA and HUMIC cake extract was reported. These results are consistent with the ones measured for C18QA in section 6.3.7. Adsorption of C18QA occurs only under liquor conditions at very high pH.

FTIR measurements were performed to investigate the adsorption of C18QA on oxalate from different solutions.

8.2 Experimental

8.2.1 Materials

Chemicals: Octadecyltrimethylammonium bromide (section 2.2.1) and HUMIC cake extract (section 3.2.3) were used.

8.2.2 Instrumental

A Perkin Elmer, System 2000, FTIR instrument (Serial No: 35191) was equipped with a MIR-TGS (deuterated triglycine sulfate) detector. The internal refraction element was made of ZnSe that was resistant to caustic. The Spectrum v2.00 software package was installed for data collection and evaluation. The beam angle was constant at 45°.

8.2.3 Conditions

Temperature: Measurements were carried out at ambient temperature.

Solutions: Synthetic liquor (section 2.2.3), 3.5 M NaOH/1.5 M NaCl and 1 M NaOH/4 M NaCl solutions were prepared and saturated with sodium oxalate at room temperature. After saturation, the solutions were purified with activated carbon and filtered.

8.2.4 Procedure

The solid sodium oxalate (5 g/L) was conditioned in solutions overnight with or without C18QA and HUMIC cake extract present. Some of the solution was discarded in order to obtain a thick suspension of sodium oxalate. The IRE was covered with the suspension and its spectrum was taken. The spectra of the matrix solutions were obtained as well. The spectrum of the C18QA adsorbed on the solid oxalate (S_{C18QA}) was calculated by subtracting the spectra of C18QA dissolved in matrix solution ($S_{QA\ sol}$) and of solid oxalate ($S_{oxalate}$) from the spectra of the suspension ($S_{QAsuspension}$):

$$S_{C18QA}=S_{QA\ suspension}-S_{oxalate}-S_{QA\ sol}$$

The spectrum of the solid oxalate, $S_{oxalate}$ was calculated from the spectra of the oxalate suspension taken without C18QA present ($S_{suspension}$) and of matrix solution ($S_{solution}$):

$$S_{oxalate}=S_{suspension}-S_{solution}$$

8.3 Results and Discussions

8.3.1 Adsorption of C18QA from solution of 1 M NaOH/4 M NaCl

The spectra of different concentrations of C18QA dissolved in solution of 1 M NaOH/4 M NaCl is shown in Figure 8.1. The characteristic peaks corresponded to the presence of C18QA appeared in the absorption spectra around 2922 cm^{-1} and 2952 cm^{-1}. Solution spectra were subtracted. The strong absorption peaks above 3000 cm^{-1} and between 1500-1800 cm^{-1} were due to water and CO_2 absorptions respectively. Figure 8.2 focuses on the part of interest of the same spectra.

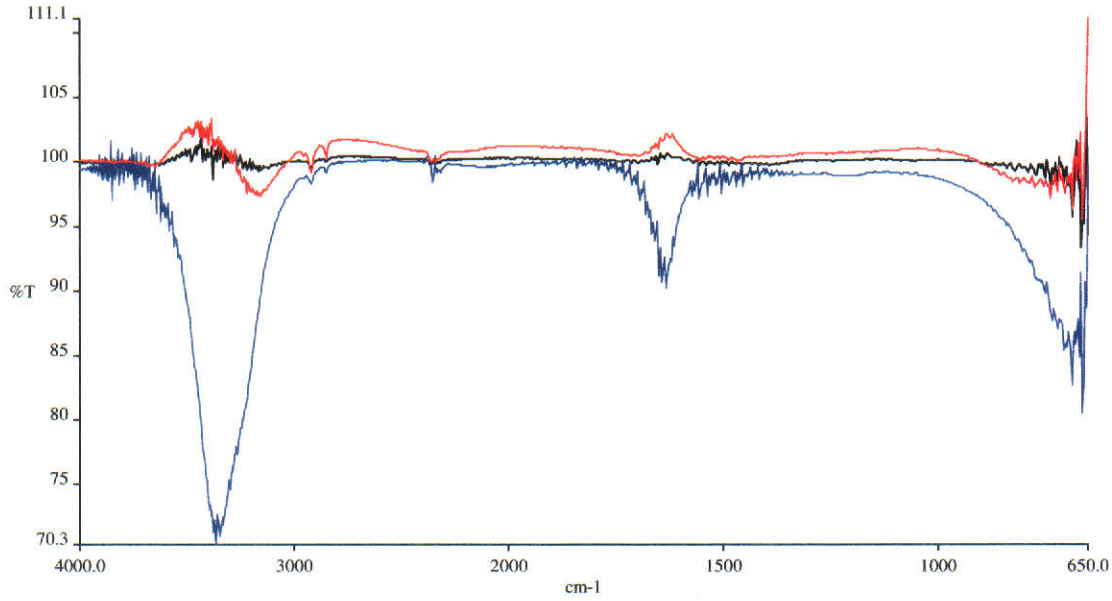

Figure 8.1: FTIR spectra of different concentrations of C18QA in solution of 1 M NaOH/4 M NaCl
(15 ppm-black, 30 ppm-blue, 60 ppm-red)

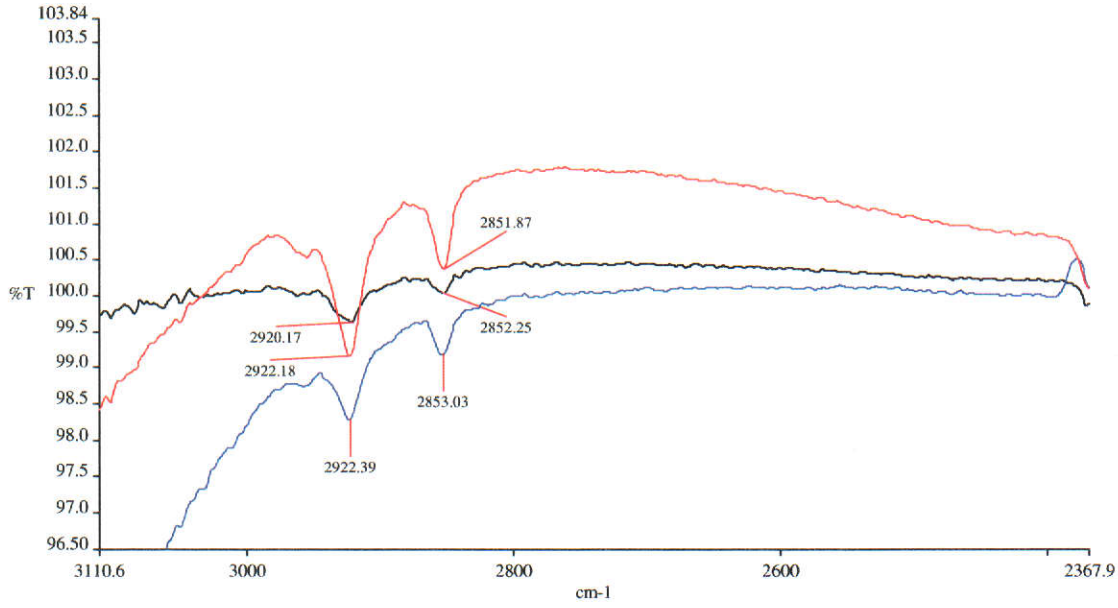

Figure 8.2: FTIR spectra of different concentrations of C18QA in solution of 1 M NaOH/4 M NaCl
(15 ppm-black, 30 ppm-blue, 60 ppm-red)

The absorptions at 2922 cm^{-1} and 2852 cm^{-1} were proportional to the concentration of C18QA in solution. Therefore, we were confident that these peaks

were the characteristic peaks of the C18QA in this solution. No other peaks were found.

Figures 8.3 and 8.4 plot the spectra of solid oxalate surface (blue), of 30 ppm C18QA present in solution (green), of oxalate suspension with C18QA adsorbed on the surface (black) and the spectrum of the C18QA adsorbed on the oxalate surface calculated from the above spectra (red).

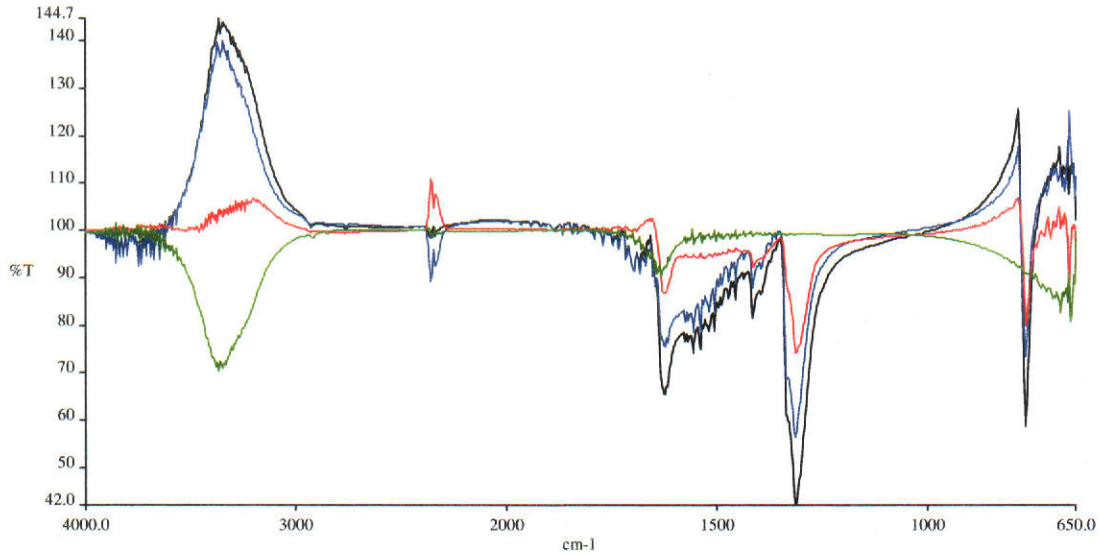

Figure 8.3: FTIR spectra of 30 ppm of C18QA in solution of 1 M NaOH/4 M NaCl (green), of solid oxalate surface (blue), of oxalate suspension with C18QA adsorbed on the surface (black) and of the C18QA adsorbed on the oxalate surface (red).

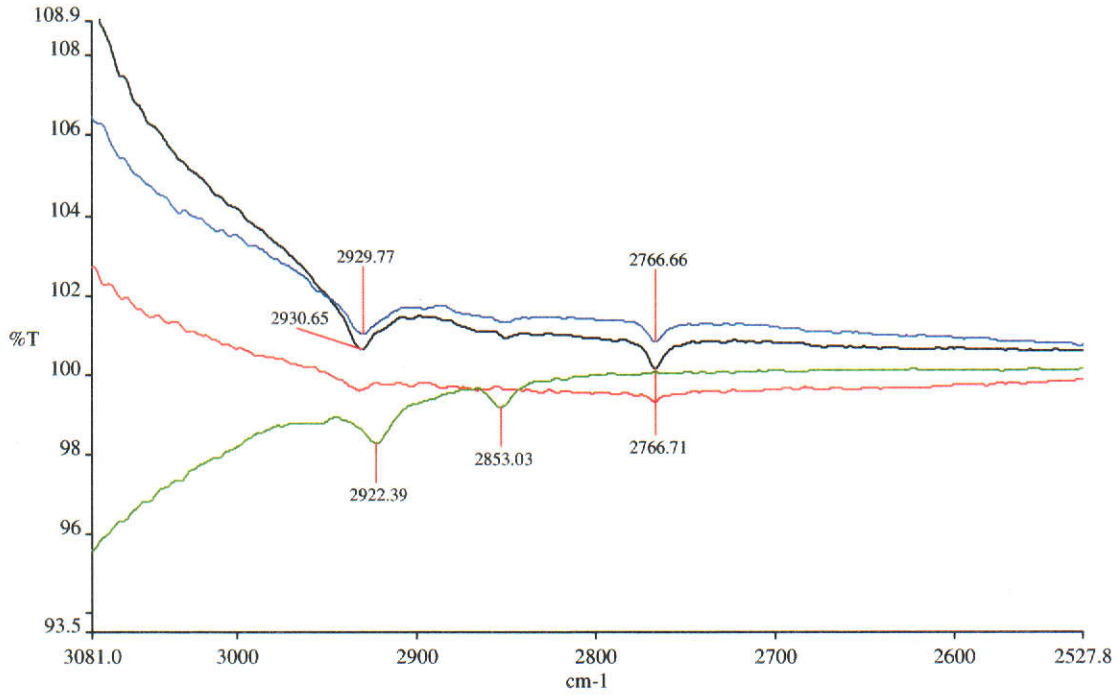

Figure 8.4: FTIR spectra of 30 ppm of C18QA in solution of 1 M NaOH/4 M NaCl (green), of solid oxalate surface (blue), of oxalate suspension with C18QA adsorbed on the surface (black) and of the C18QA adsorbed on the oxalate surface (red).

The characteristic peak of C18QA was around 2930 cm^{-1} when measured in suspension. Although, the C18QA obviously gave a signal in this system, no C18QA was adsorbed on the surface of sodium oxalate (red line in Figure 8.4). This result was consistent with findings in section 6.3.7.

8.3.2 Adsorption of C18QA from solution of 3.5 M NaOH/1.5 M NaCl

The spectra of different concentrations of C18QA dissolved in solution of 3.5 M NaOH/1.5 M NaCl are shown in Figures 8.5 and 8.6. The characteristic peaks corresponded to the presence of C18QA appeared in the absorption spectra around 2920 cm^{-1} and 2951-2952 cm^{-1}. Solution spectra were subtracted.

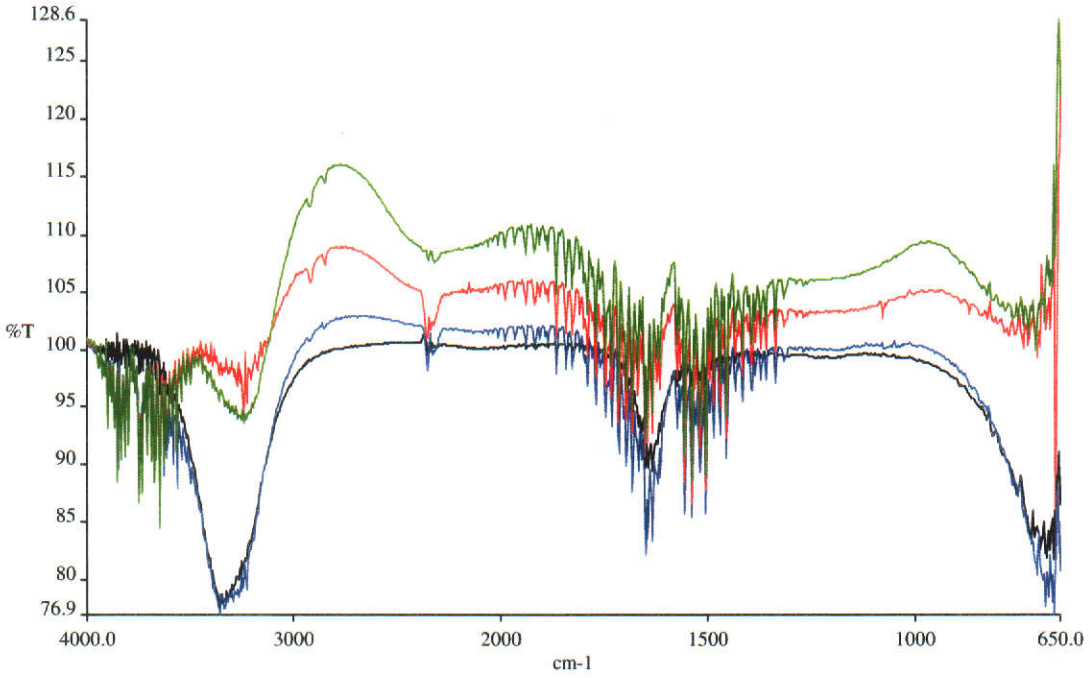

Figure 8.5: FTIR spectra of different concentrations of C18QA in solution of 3.5 M NaOH/1.5 M NaCl

(30 ppm-black, 60 ppm-blue, 100 ppm-red, 200 ppm-green)

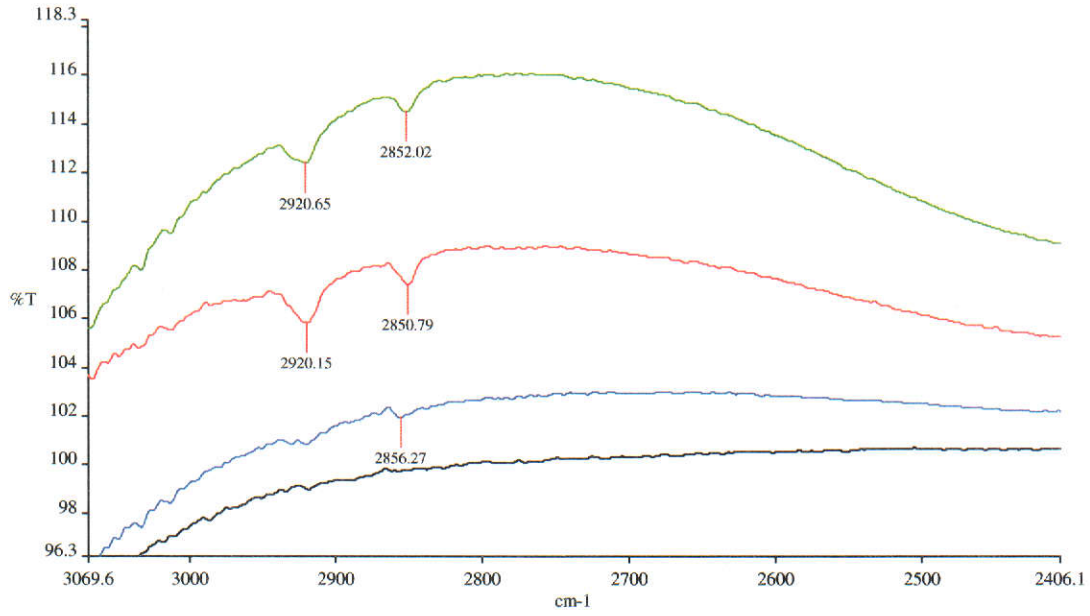

Figure 8.6: FTIR spectra of different concentrations of C18QA in solution of 3.5 M NaOH/1.5 M NaCl

(30 ppm-black, 60 ppm-blue, 100 ppm-red, 200 ppm-green)

The intensities of absorption peaks at 2920 cm^{-1} and 2851-2852 cm^{-1} were proportional to the concentration of C18QA in solution. However, the detection limit of the measurement was much higher than in solution of 1 M NaOH/4 M NaCl. Only concentrations of C18QA above 60 ppm could be detected.

Figures 8.7 and 8.8 plot the spectra of solid oxalate surface (blue), of 100 ppm C18QA present in solution (black), of oxalate suspension with C18QA adsorbed on the surface (red) and the spectrum of the C18QA adsorbed on the oxalate surface calculated from the above spectra (green).

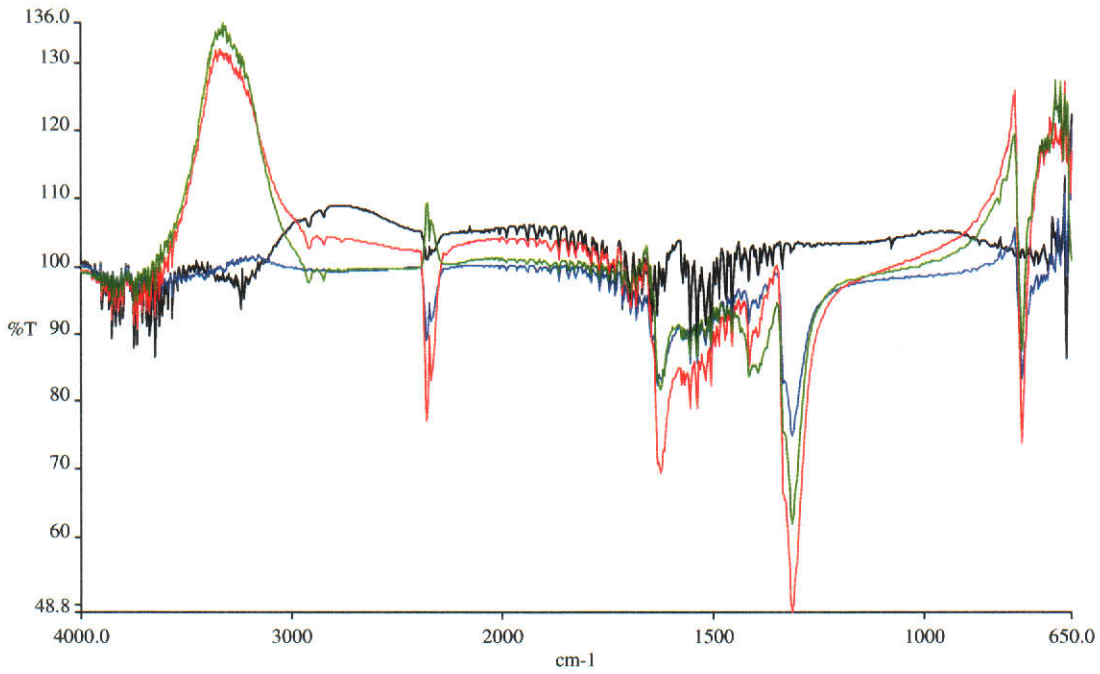

Figure 8.7: FTIR spectra of 100 ppm of C18QA in solution of 3.5 M NaOH/1.5 M NaCl (black), of solid oxalate surface (blue), of oxalate suspension with C18QA adsorbed on the surface (red) and of the C18QA adsorbed on the oxalate surface (green).

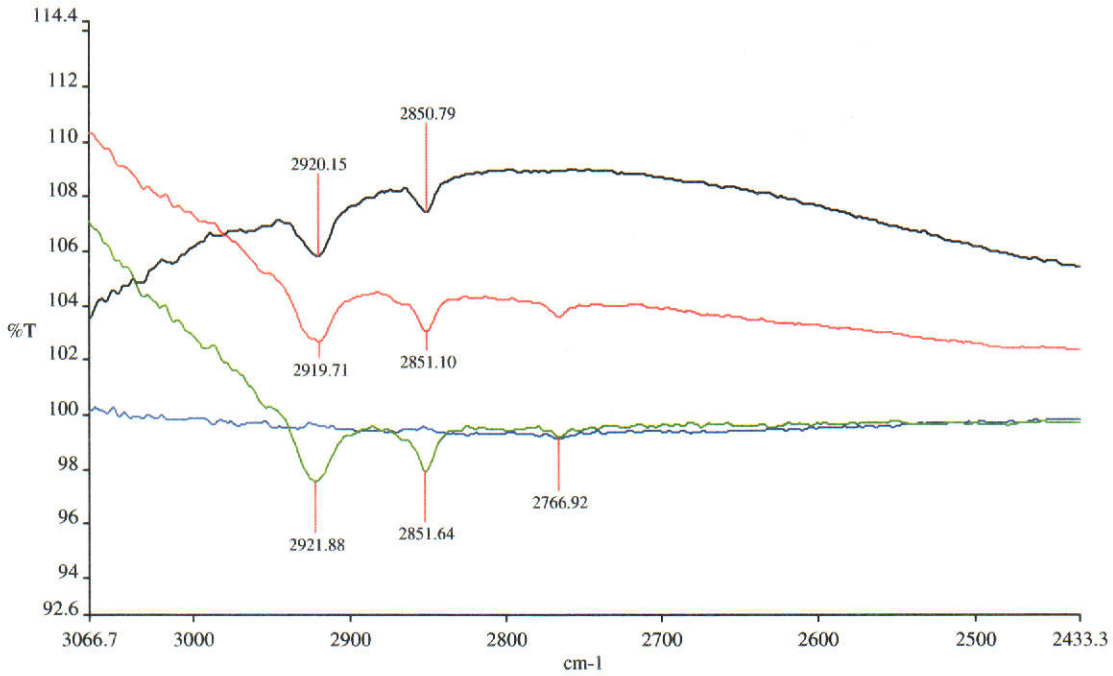

Figure 8.8: FTIR spectra of 100 ppm of C18QA in solution of 3.5 M NaOH/1.5 M NaCl (black), of solid oxalate surface (blue), of oxalate suspension with C18QA adsorbed on the surface (red) and of the C18QA adsorbed on the oxalate surface (green).

The characteristic peaks of C18QA were 2920 cm^{-1} and 2851 cm^{-1} when measured in suspension. These wave numbers are lower than the ones in solution of 1 M NaOH/4 M NaCl. Adsorption of C18QA was found on the surface of sodium oxalate in this system (green line in Figure 8.8). This result was consistent with findings in section 6.3.7.

8.3.3 Adsorption of C18QA from synthetic liquor

The spectra of different concentrations of C18QA dissolved in synthetic liquor are shown in Figures 8.9 and 8.10. The characteristic peaks related to the presence of C18QA appeared in the absorption spectra around 2919 cm^{-1} and 2851 cm^{-1}. Solution spectra were subtracted.

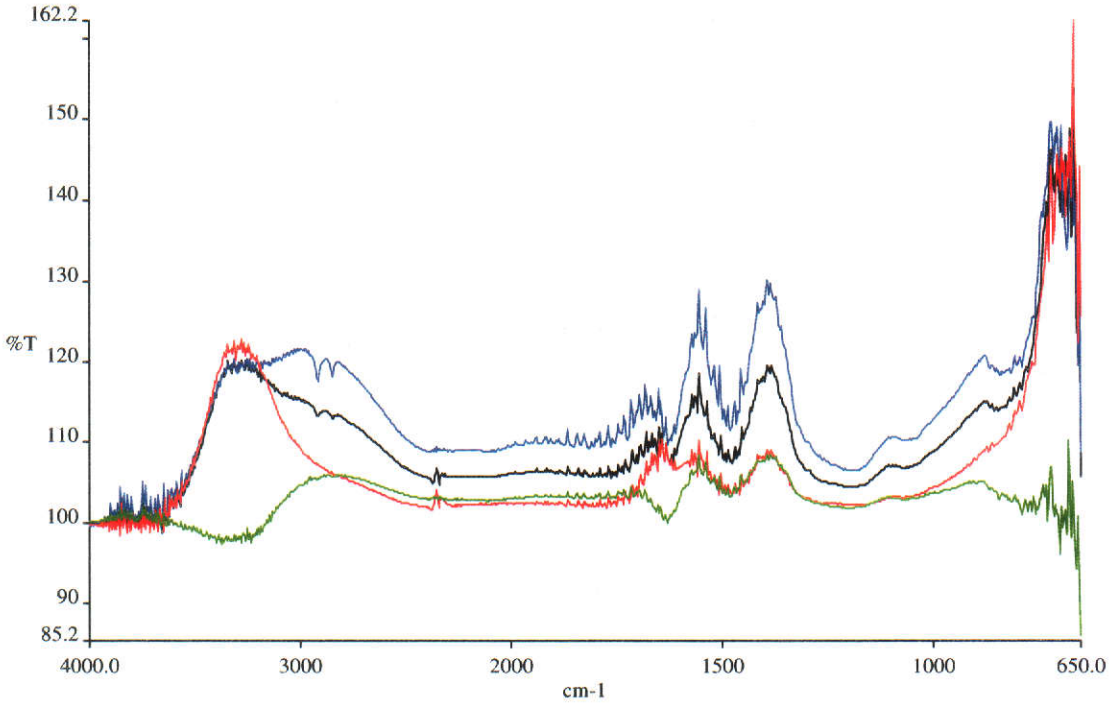

Figure 8.9: FTIR spectra of different concentrations of C18QA in synthetic liquor (30 ppm-red, 60 ppm-green, 100 ppm-black, 150 ppm-blue)

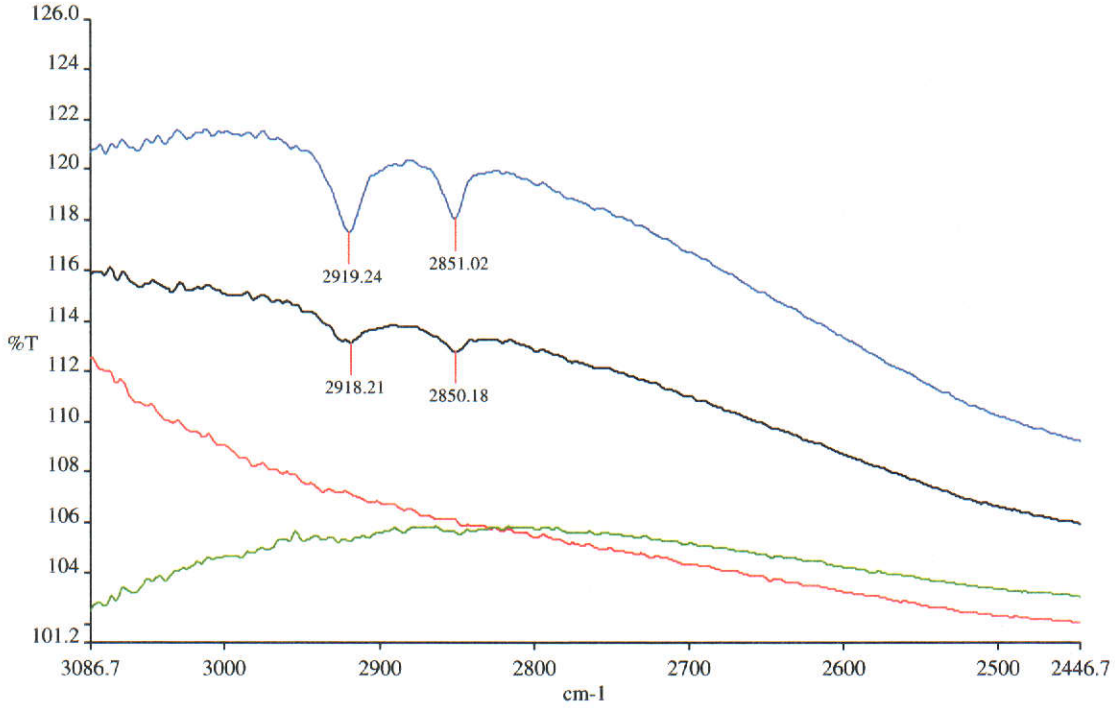

Figure 8.10: FTIR spectra of different concentrations of C18QA in synthetic liquor (30 ppm-red, 60 ppm-green, 100 ppm-black, 150 ppm-blue)

The intensity of absorption peaks at 2919 cm^{-1} and at 2851 cm^{-1} was proportional to the concentration of C18QA in solution. The detection limit of the measurement was higher than that in solution of 3.5 M NaOH/1.5 M NaCl. Only concentrations of C18QA equal or above 100 ppm could be detected.

Figures 8.11 and 8.12 plot the spectra of solid oxalate surface (blue), of 150 ppm C18QA present in solution (black), of oxalate suspension with C18QA adsorbed on the surface (green) and the spectrum of the C18QA adsorbed on the oxalate surface calculated from the above spectra (red).

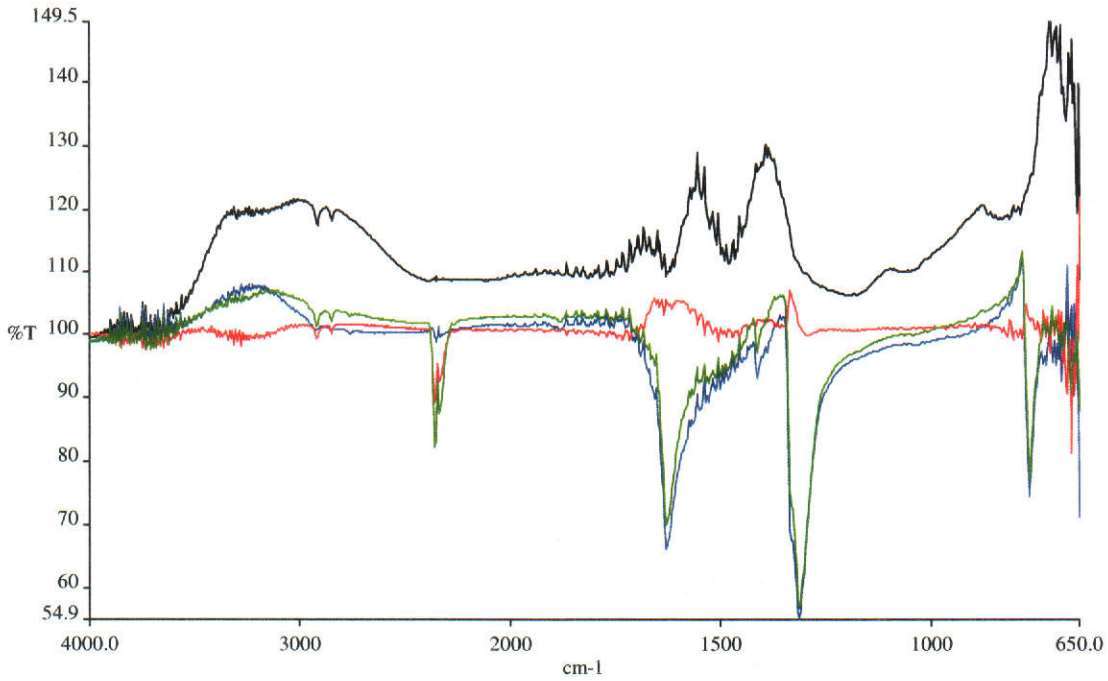

Figure 8.11: FTIR spectra of 150 ppm of C18QA in synthetic liquor (black), of solid oxalate surface (blue), of oxalate suspension with C18QA adsorbed on the surface (green) and of the C18QA adsorbed on the oxalate surface (red).

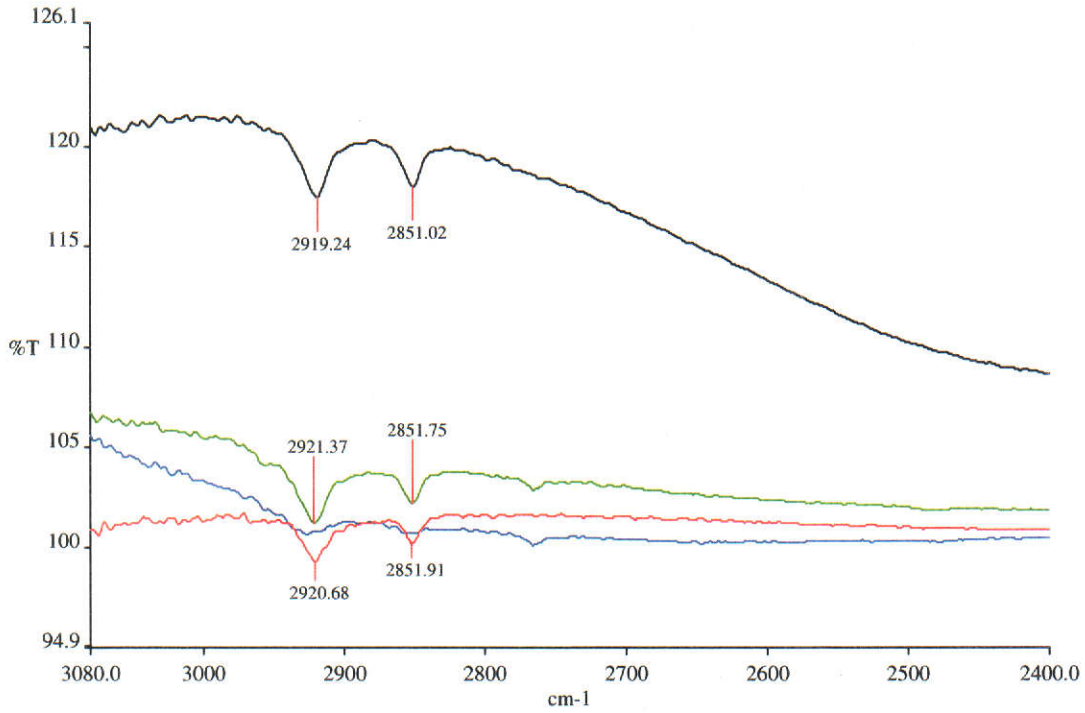

Figure 8.12: FTIR spectra of 150 ppm of C18QA in synthetic liquor (black), of solid oxalate surface (blue), of oxalate suspension with C18QA adsorbed on the surface (green) and of the C18QA adsorbed on the oxalate surface (red).

The characteristic peak of C18QA was 2921 cm^{-1} and 2952 cm^{-1} when measured in suspension. These wave numbers are similar to those found in solution of 3.5 M NaOH/1.5 M NaCl. Adsorption of C18QA was found on the surface of sodium oxalate in this system (red line in Figure 8.12). This result was consistent with findings in section 6.3.7.

8.3.4 Adsorption of HUMIC cake extract from synthetic liquor

The adsorption of HUMIC cake extract was also investigated. The spectra of different concentrations of HUMIC cake extract in synthetic liquor are shown in Figures 8.13 and 8.14. The characteristic peaks related to the presence of humic material appeared in the absorption spectra at 2920-2930 cm^{-1} and at 2954-2956 cm^{-1}. These wave numbers are very close to the characteristic peaks of C18QA. This suggests that the CH_2 groups are responsible for the infrared absorption in both C18QA and HUMIC cake extract organic compounds.

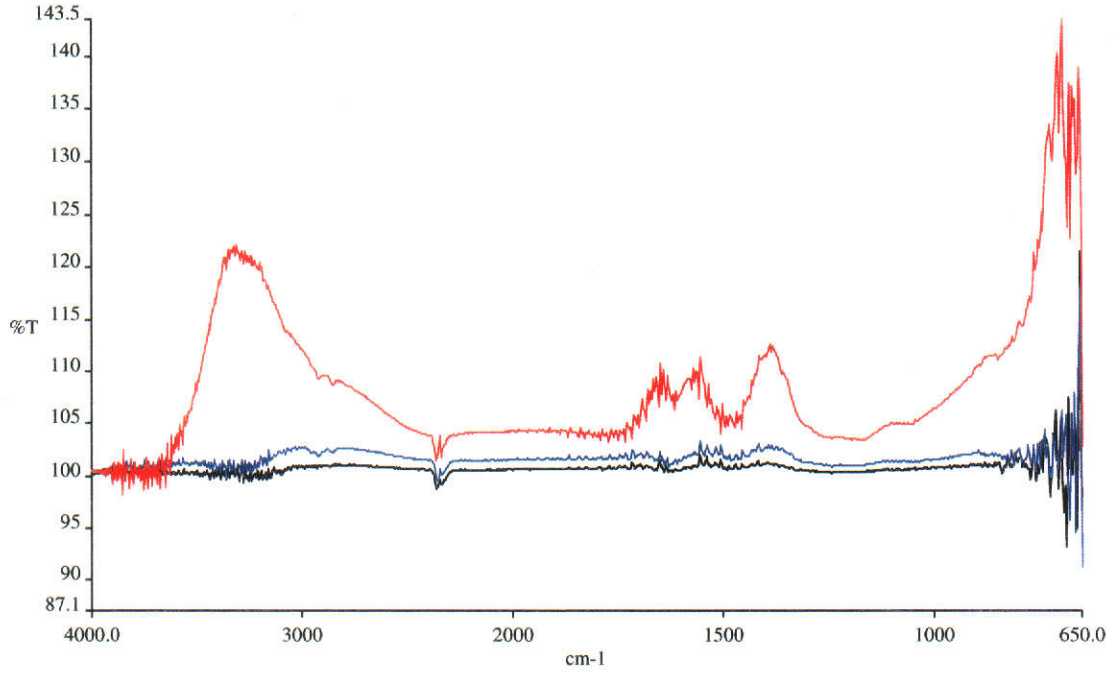

Figure 8.13: FTIR spectra of different concentrations of HUMIC cake extract in synthetic liquor

(10 g/L-black, 20 g/L-blue, 50 g/L-red)

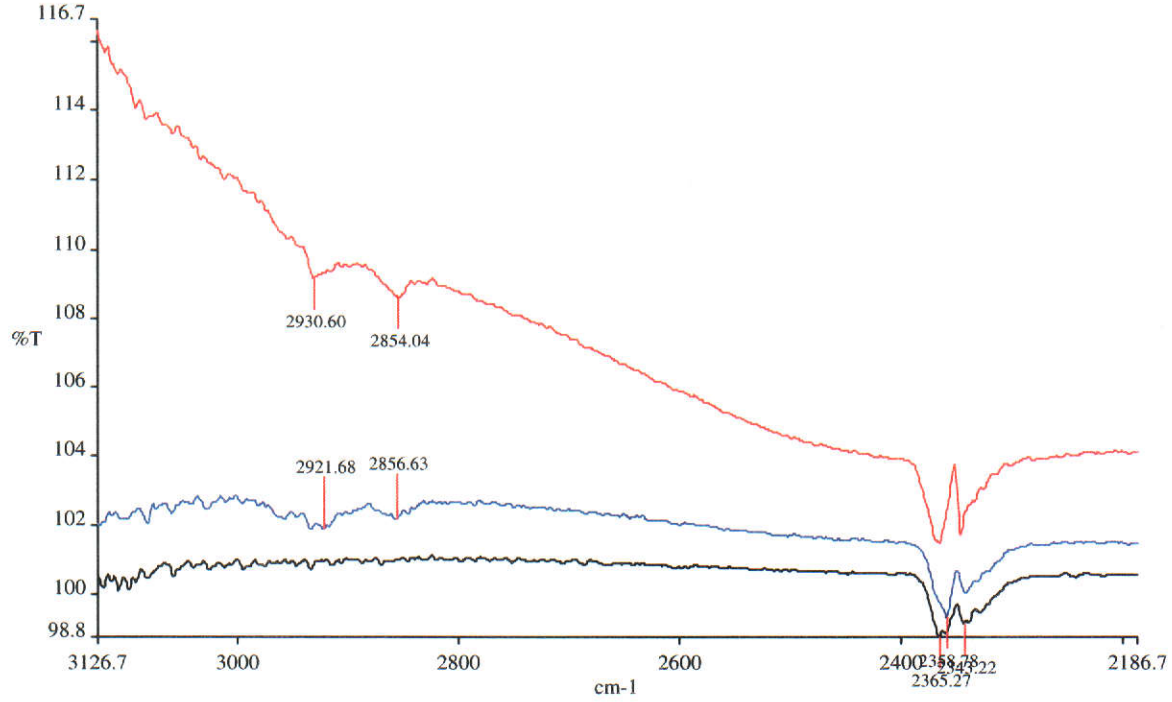

Figure 8.14: FTIR spectra of different concentrations of HUMIC cake extract in synthetic liquor

(10 g/L-black, 20 g/L-blue, 50 g/L-red)

The absorption peaks appeared at 2930 cm^{-1} and at 2854 cm^{-1}, and they were proportional to the concentration of HUMIC cake extract in solution. The detection limit of the measurement was 20 g/L. Only concentrations of HUMIC cake extract equal or above 20 g/L could be detected.

Figures 8.15 and 8.16 plot the spectra of solid oxalate surface (green), of 10 g/L HUMIC cake extract present in solution (red), of oxalate suspension with HUMIC cake extract adsorbed on the surface (blue) and the spectrum of the HUMIC cake extract adsorbed on the oxalate surface calculated from the above spectra (black).

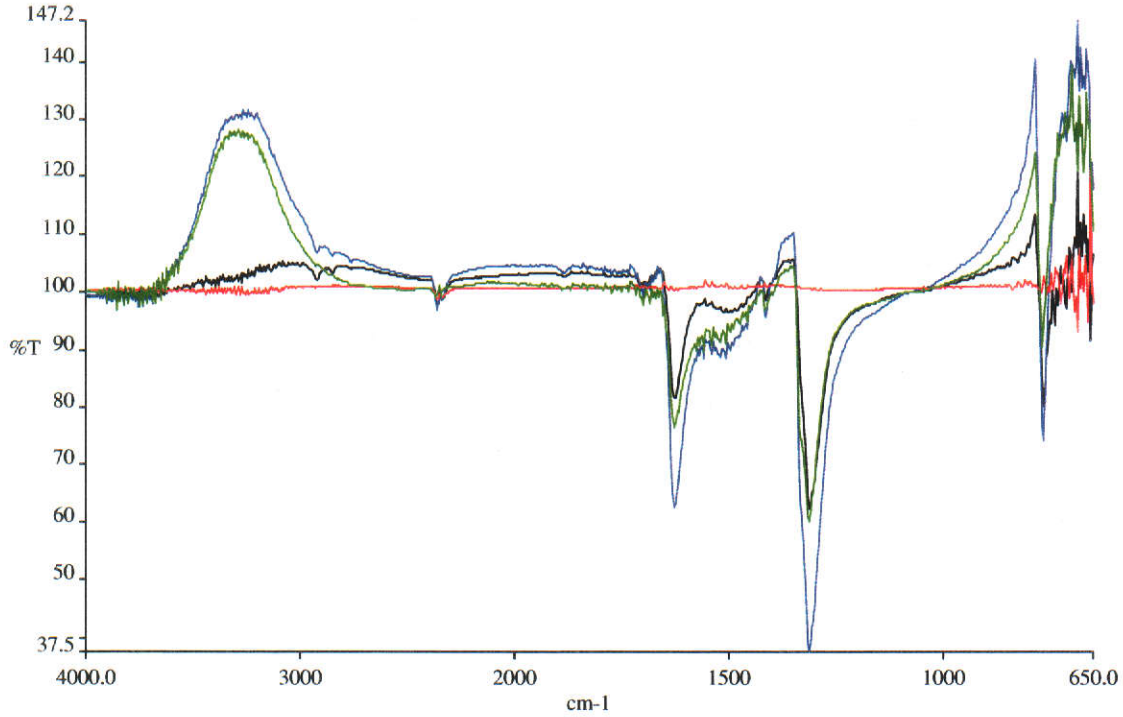

Figure 8.15: FTIR spectra of 10 g/L of HUMIC cake extract in synthetic liquor (red), of solid oxalate surface (green), of oxalate suspension with HUMIC cake extract adsorbed on the surface (blue) and of the HUMIC cake extract adsorbed on the oxalate surface (black).

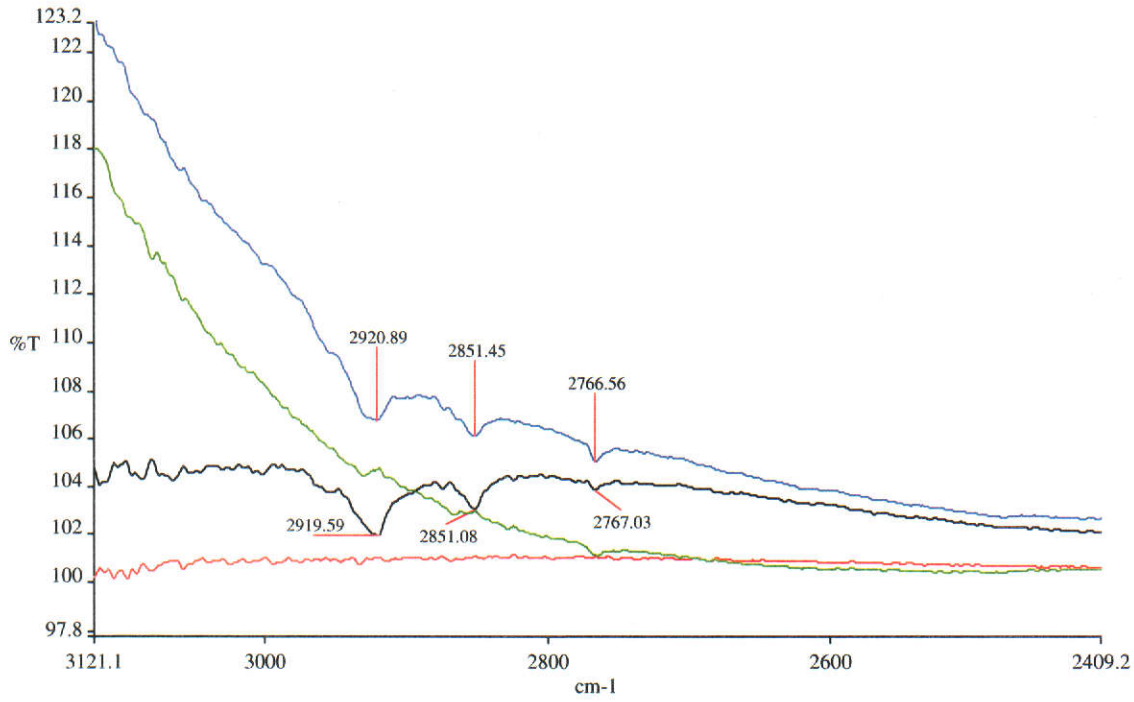

Figure 8.16: FTIR spectra of 10 g/L of HUMIC cake extract in synthetic liquor (red), of solid oxalate surface (green), of oxalate suspension with HUMIC cake extract adsorbed on the surface (blue) and of the HUMIC cake extract adsorbed on the oxalate surface (black).

The characteristic peaks of HUMIC cake extract were 2920 cm^{-1} and 2951 cm^{-1} when adsorbed. These wave numbers are exactly the same than those measured for C18QA. Adsorption of HUMIC cake extract was found on the surface of sodium oxalate in synthetic liquor (black line in Figure 8.16). This result was consistent with findings in section 6.3.7.

As the characteristic absorption peaks were the same for both C18QA and HUMIC cake extract, there was no point to measure adsorption from a mixture of these chemicals with FTIR.

8.4 Conclusions and Recommendations

8.4.1 Conclusions

FTIR measurements were performed to investigate the adsorption of C18QA on solid oxalate in synthetic liquor, in 3.5 M NaOH/1.5 M NaCl and in 1 M NaOH/4 M NaCl solutions. The aim of the measurements was to develop a technique suitable for FTIR measurements of C18QA adsorbed at the solid/liquid

interface in synthetic liquor. Adsorption from other solutions was measured for comparison.

In 1 M NaOH/4 M NaCl solution, 15 ppm of C18QA was detectable. The characteristic peaks appeared at 2922 cm^{-1} and 2852 cm^{-1}. No adsorption of C18QA on oxalate was found, and this was consistent with the result from direct adsorption measurement

In 3.5 M NaOH/1.5 M NaCl solution, the detection limit was increased to 60 ppm. The characteristic peaks were shifted to lower wave numbers, 2920 cm^{-1} and 2851 cm^{-1}. Adsorption of C18QA on solid oxalate was found from this solution. This is also consistent with results obtained with direct adsorption measurements (section 6.3.7).

In synthetic liquor, the peaks were shifted to 2921 cm^{-1} and 2852 cm^{-1}, and the detection limit was increased to 100 ppm. In good agreement with previous results, adsorption of C18QA on solid oxalate was found in synthetic liquor.

The adsorption of HUMIC cake extract was seen as well. The characteristic peaks for humic material and C18QA appeared at the same wave numbers when adsorbed on oxalate.

Unfortunately, these results were not informative for the nature of adsorption as the detection limit was much higher than the concentration range covered in direct adsorption isotherm measurements. However, results confirmed that the adsorption of C18QA and HUMIC cake extract occured from synthetic liquor, and the C18QA adsorption on oxalate was pH dependent.

8.4.2 Recommendations

FTIR has the potential to give information on the structure of the adsorbed molecules. The detection limit of FTIR measurements in synthetic liquor, however, was very high. The peaks were not well developed, therefore, any conclusion on the nature of the adsorbed layer would be unsupported.

More work would be required to improve the capacity of the instrument. For instance, a thicker suspension could be prepared or instrument parameters, such as scan number or more sensitive detector, should be changed for future work.

Chapter 9

Conclusions

During the three year study, it was possible to gain more knowledge about the action of stabilizers and clarify the reasons behind many phenomena experienced with stabilizers. However, this research has also brought up new questions and new problems to resolve. Very often, this study commenced a new research track that would have been beneficial to follow, but it was stopped, because it would have led too far from the original problem. Due to the timeframe given for this research and the, sometimes, strict industrial demand towards the possible outcome of this research avoiding confidentiality issues, focus was concentrated on the direction which would most likely lead to the answers to the original questions. Accordingly, and regrettably, it was necessary to stop examining systems that would have been scientifically very interesting and novel, but would have consumed much time or would have taken the research to fields far away from the proposed research program.

This chapter aims to be a summary of the work done so far, outlining the results achieved, interpreting the questions that arose and giving suggestions for the direction of possible future work.

The aim of this project has been to investigate how stabilizer molecules affect the precipitation of sodium oxalate and to understand the mechanisms by which specific additive molecules stabilize a high level of supersaturation of sodium oxalate in Bayer liquors in the presence of sodium oxalate seed.

Previously, quaternary amines were found to be effective oxalate stabilizers in plant process liquors (Farquharson *et al.* 1995b); they increased the stability of liquor, the highest oxalate concentration that the liquor can tolerate without co-precipitation for 24 hours. The effect of QAs on liquor stability was determined with the MOST test. This test simulated plant conditions (ie alumina trihydrate and sodium oxalate crystals were present). However, the concentration of solid oxalate in this system was very low. It has not been clarified whether this test measured the nucleation or crystal growth of sodium oxalate, or both simultaneously occurred

during the test. Moreover, the QAs tested with MOST tests were commercial grade products. As oxalate seed is always present in the hydrate precipitators, the principal aim of this work was to determine the effect of QAs on oxalate crystallization. Accordingly, QAs were tested in MOSPIT tests (Miniaturised Oxalate Seed Poison Impact Test), which clearly measured the effect of QAs on the crystal growth of sodium oxalate (McKinnon *et al.* 1998). It was decided to test the active components of the commercial products used in MOST tests. If the active component of the tested commercial product was not available as a pure chemical with more than 95% purity, a chemically similar compound with acceptable purity was chosen.

At the beginning of the work, it was important to test different containers for suitability. MOSPIT results measured in different containers revealed that the test gives an anomalous response when carried out in polypropylene test tubes. Results indicated that the extremely high pH of the liquor attacked the plastic material, causing false test results. As the result of this observation, all of the plastic and rubber materials being in contact with liquor, especially when the liquor was hot, were tested prior to use. During this work, glass and steel vessels were used in experiments. It would be interesting to identify the contamination leaching out of the polypropylene, as it is extremely efficient, together with QAs, as a stabilizer.

QAs were classified as strong, medium or weak crystal growth inhibitors in plant liquor using the MOSPIT test. All of the QAs tested had an effect on the oxalate yield. Results showed that the order of the strength of QAs followed the same trend in both MOST and MOSPIT tests. Many QAs were found to be more effective in plant liquor than the N138 product that has been currently used in the plant. From the chemical point of view, C18QA, C16QA, C14QA, C12QA or C16EtQA should be more favoured as an additive into the process liquor to stabilize oxalate. Commercial considerations may, however, dictate otherwise..

As the characteristics of a plant liquor change day to day in a plant, depending on the operation conditions and the bauxite quality, it was decided to use synthetic liquor of constant composition in order to clarify the action of QAs in liquor and to obtain consistent data. However, QAs did not inhibit oxalate crystal growth in synthetic liquor. This must have been due to one of the two differences between synthetic and plant liquors, the absence of plant organics or trace elements. The influence of plant organics was more likely.

One way to increase the organic content of the liquor was to make up blends of synthetic and plant liquors. QAs were tested in these blends and were found to be effective inhibitors. It was discovered that a small amount of plant organics was sufficient to induce the inhibitory effect of QAs. These results confirmed that plant organics play an important role in the action of QAs in plant liquor. The reason that QAs inhibit crystal growth in plant liquor and blend liquors must be due to synergy with some of the organic content of the plant liquor. It was decided to examine the effect of QAs in the presence of plant organics and model organics. Organics trapped in the solid sodium oxalate precipitated in plant (Oxalate Belt Filter Cake) or dissolved in the plant process liquor were extracted and fractionated. Three fractions were obtained, humic, low molecular weight and fulvic fractions. Extracts could be further fractionated, for instance, based on molecular weight. That would give more detailed classification. QAs were repeatedly tested using the MOSPIT test in the presence of these extracts. The impact of extracts in the absence of QAs on oxalate crystal growth was measured as well.

Results confirmed that the presence of plant organics was essential to induce the inhibitory effect of QAs. Both the HUMIC and LMW extracts inhibited oxalate crystal growth in synthetic liquor. The decrease in yield was proportional to the concentration of organics. However, the addition of QAs into the liquor solution of these extracts resulted in an enhanced crystal growth inhibition. In the presence of humates, the additional effect of QAs was proportional to the QA concentration and to the humate concentration. However, in the presence of LMW extracts, the high concentration of QAs often reversed the enhanced inhibitory effect of QAs found at low concentrations. This behaviour was confirmed with other anionic surfactant type compounds of low molecular weight. One possible explanation of this reversed effect is that the QAs present at concentrations higher than the CMC will solubilise organics adsorbed previously on the solid oxalate surface in micelles in solution.

Since only a few components of the extracts have been identified, and they are commercially sensitive, a series of chemicals that have some of the characteristics of the extracts were tested. The impact of QAs on sodium oxalate crystal growth was determined in the presence of these chemicals at various concentration ratios. Many of the tested non-Bayer chemicals (TABLES II & III) were found to be effective oxalate poisons at given concentrations. However, an enhanced inhibition of oxalate crystal growth in the presence of QAs was observed in a few instances only.

The commercial (non-Bayer) humics tested had an impact on oxalate yield, but the synergistic effect with QAs only appeared after the degradation of these materials at high temperature in liquor. The degraded materials resulted in the same inhibitory effect but at much higher concentrations than the non-degraded ones. The analysis of the humic liquor solutions before and after degradation did not show LMW contaminations at a significant level and the LMW concentrations did not change during the degradation. Compounds in the LMW extract are the low molecular weight intermediates of degradation of humic materials. The degradation of the commercial humics probably resulted in intermediates that still had high molecular weight, therefore, they were humic-type material. The chemical effects of the degradation on the commercial humics have not been identified in this case. Generally, the degradation of organics results in the oxidation of the carbon atoms of the carbon chain. Carbon atoms of low oxidation number, such as with double bonds, will break and carboxylate or hydroxyl groups are formed.

Polyacrylate, sodium dodecyl sulfate, sodium dodecylbenzenesulfonate and Triton X-100 showed synergy with QAs.

Some LMW compounds were tested as well. Synergy between decanoic acid and C12QA, oleic acid and C16PyrQA, stearic acid and C18QA or N138# were found. Due to the confidential nature of the tested LMW-OSPs, these compounds and the LMW extract were not investigated further within the PhD project.

From the results measured up to date, desired features of the organics that interact with QAs to produce an enhanced inhibitory effect can be defined.

a) The organics have to be oxalate poisons. Without exception, all of the organics that showed synergy with QAs inhibited crystal growth of sodium oxalate.
b) The surfactant nature of the organics seems to be crucial. Having other characteristics, such as high molecular weight, similar functional groups as humates were not enough to induce the action of QAs.

QAs behave differently in the presence of different extracts. The fulvic plant and cake extracts have not been investigated, and neither has the mixture of extracts. It would be interesting to compare the effects of mixtures with the effects of individual components.

The synergy found between plant organics and QAs is quite interesting. The nature of interaction between QAs and plant organics is not clear. More work would be required for a better understanding of the attraction between QAs and individual plant organics in liquor solutions. Another interesting question is how the excess of these extracts in plant liquor would affect the action of QAs. When the ratio of fractions of plant organics is unbalanced, QAs might give a response different from that measured in plant liquor. These questions are out of the scope of this work; nevertheless, further investigations would lead to a better knowledge of the role of plant organics in the process and of the action of QAs in different types of liquors.

It was thought that the inhibition of crystal growth of sodium oxalate measured in the presence of certain organics and QAs was probably due to the adsorption of these chemicals onto the oxalate surface. Hopefully, knowing the adsorption behaviour of QAs and organics under different conditions at a molecular level would lead us to understand the inhibitory effect of QAs and organics measured macroscopically. It was planned, as part of the original proposal, to measure adsorption isotherms of QAs on sodium oxalate in synthetic liquor, and for this, it was necessary to be able to measure concentrations of QAs in liquor. The strongest crystal growth inhibitor was found to be the C18QA; consequently, it was decided to examine the adsorption character of this surfactant in detail. Accordingly, the analysis method had to be suitably specific for the analysis of this surfactant. A method developed by Hind, Bhargava & Grocott (1997a) for the determination of QAs (C12QA, C14QA and C16QA) in liquor samples was employed. Preliminary laboratory tests showed that this method was suitable for the analysis of C18QA as well.

While low recovery and non-linear calibration curves at concentrations above 5 ppm were reported in the original method, significant improvement of the method was achieved. With the addition of an internal standard very similar chemically to the analyte, the calibration curve became linear up to 250 ppm (1000 ng). That enabled the elimination of a sub-sampling step in adsorption isotherm measurements. The method was modified in order to analyse C18QA from sodium oxalate solutions with pH much lower than in liquors. With this modified method, it was possible to determine C18QA adsorbed on the surface of solid oxalate directly. Significant improvement was achieved regarding the storage of samples. The reference compounds were found to be unstable in dichloromethane, other solvents had to be

tested. Chloroform was found to be suitable for storage and as a carrier for the GC-FID. Although attempts were made, it was very difficult to improve the precision of the method any further. The standard deviation was determined to be 7-10 % for concentrations between 0-20 ppm. An attempt was made to apply the conditions developed above for the determination of other QAs, such as C12QA, C16PyrQA or N138#. It was evident from the results that the same conditions could not be used for the analysis of those QAs. For instance, N138# did not give any signal on the GC-FID. It seems that the optimum conditions for the analysis of QAs should be worked out individually in future work.

The adsorption isotherm at a solid/liquid interface represents the amount of adsorbate adsorbed on a unit of surface of the adsorbent as a function of the concentration (activity) of the adsorbate in solution. Then, every process that influences the surface concentration or the concentration of free adsorbate in solution affects the adsorption isotherm. Dealing with surfactants, the most obvious process affecting the surfactant concentration in solution is micelle formation. The CMC (critical micelle concentration) is a significant point on the adsorption isotherm. This point represents the concentration above which micelles exist in solution. Usually, there is a knee in the adsorption isotherm at this concentration, due to the fact that the concentration of free molecules in solution remains constant above the CMC.

The primary aim of surface tension measurements was to determine the CMC of C18QA so as interpret the adsorption isotherm of this quaternary amine. The CMC of C18QA that was determined from the surface tension vs. surfactant concentration plot was 1.5 ppm in liquor containing 0.722 g/L sodium oxalate, 5 g/L sodium malonate and 15 g/L sodium succinate in addition to the inorganic components. The effects of QAs other than C18QA on the surface tension of liquor were investigated for comparison. It was evident from the measurements that an interaction exists between QAs and the di-carboxylate components of the synthetic liquor. This interaction is probably due to the very high ionic strength of the solution. Calculations show that the amount of water in synthetic liquor is not sufficient to form entire hydrate cells around the ions, therefore, ion-associations are highly favoured in this solution. Unfortunately, further investigation of this phenomenon was not possible within this project.

Results revealed that the CMC of QAs in liquors depended on the composition of synthetic liquor. Not only did the ionic strength influence the CMC, for example in diluted solutions, specific anions also had direct interactions with quaternary amines. It is recommended that the CMC of QAs should be given together with the exact composition of the liquors in the future. Particularly, the sodium oxalate, sodium malonate and sodium succinate components seem to be crucial.

It was found that QAs inhibited oxalate crystal growth in plant liquors and in synthetic liquors in the presence of certain organics. The effect of QAs measured macroscopically certainly has an explanation at a molecular level. It was thought that adsorption measurements could lead to an understanding of the mechanisms by which QAs affect oxalate crystallization.

Since a method was established for its analysis, the adsorption behaviour of the strongest crystal growth inhibitor, C18QA was investigated with and without the presence of the HUMIC cake extract. Since it was shown that plant organics were necessary for the action of QAs, and the humic material was especially effective in this role, it was decided to measure the adsorption behaviour of the HUMIC cake extract as well. It was planned to measure the adsorption isotherms of both, the C18QA and HUMIC cake extract individually and also that from a mixture of the C18QA and the HUMIC cake extract.

An adsorption procedure was developed for C18QA and for the HUMIC cake extract. The sufficient adsorption time to reach equilibrium from a mixture of C18QA and the HUMIC cake extract was established and set to 20 hours. The chemical stability of the HUMIC cake extract for the adsorption period was checked and found satisfactory. No significant adsorption of C18QA was measured on the glass surface of the container. The precision of the adsorption measurement from a solution of the individual components or from a mixture of C18QA and the HUMIC cake extract was found to be 25 RSD% and the recovery was 70-115%.

Contrary to the fact that QAs did not inhibit crystal growth of sodium oxalate in synthetic liquor, an adsorption isotherm of C18QA was successfully generated on acicular sodium oxalate. The adsorption isotherm conformed to Langmuir-type adsorption behaviour with 8.4×10^6 L/mol adsorption affinity and 5.6×10^{-6} mol/m^2 adsorption capacity. However, the adsorption isotherm was found to be dependent on the solid oxalate concentration. Investigations were undertaken to clarify the reason of this unusual dependence on the solid content. These investigations covered

the possibility of insufficient dispersion of solid oxalate and of pre-adsorption of a third participant that promoted the adsorption of C18QA. However, the solid oxalate was found to be well dispersed in liquor. Although calcium adsorption onto oxalate was found previously, no difference in adsorption of C18QA was measured at different calcium concentrations. The minor component responsible for the C18QA adsorption isotherm being dependent on solid concentrations could not be identified. Adsorption measurements of C18QA in different solutions, however, revealed that an extremely high pH was essential for this third participant, presumably an organic compound, to interact.

Plant humates were shown to be good crystal growth inhibitors of sodium oxalate. Accordingly, adsorption of the HUMIC cake extract on solid oxalate was expected and measured successfully. The adsorption isotherm shows a continuous increase of humic substances on the oxalate surface with increasing humic concentration in liquor. The adsorption of higher molecular weight components of the mixture of organics in the HUMIC cake extract, measured at high wavelengths, was more extensive.

The simultaneous adsorption of both C18QA and HUMIC cake extract was measured from a mixture of these components. It was found that these components enhanced the adsorption of each other. Significantly more C18QA and humates were adsorbed on the solid oxalate from a mixture than from equivalent solutions of the individual components. This co-adsorption was probably the result of an electrostatic interaction between the positively charged C18QA and the negatively charged humic material on the surface of solid oxalate. Further investigations revealed that this interaction existed between QAs and HUMIC cake extract in liquor solutions at high concentrations of the components. It was concluded that the effect of C18QA on oxalate crystallization in the presence of HUMIC cake extract was to precipitate humic material from solution onto the oxalate surface. This was possible at a much lower concentration of components when solid oxalate was present, for the adsorption concentrated the participants on the surface of oxalate, therefore the solubility product could be reached locally.

A question arose whether the adsorbed C18QA played an active role in the inhibition of oxalate crystal growth or simply modified the impact of the HUMIC cake extract on oxalate crystallization. The amount of HUMIC cake extract adsorbed from solution was compared with the corresponding oxalate yield. It was seen that

solutions containing QAs resulted in a lower level of growth inhibition than was expected on the basis of the amount of HUMIC cake extract adsorbed. This implied that the excess HUMIC cake extract did not adsorb in the same way as the humates without QA, or alternatively occupied less active growing sites, resulting in a less efficient inhibition of oxalate crystal growth. This theory was confirmed with confocal laser scanning microscopy (CLSM) measurements.

Beside C18QA, only N138# co-adsorption with the HUMIC cake extract was measured. The behaviour of this surfactant was very similar to that of C18QA. It would be interesting to compare all of the QAs regarding their adsorption characteristics and the amount of humates adsorbed together with the QAs onto the oxalate surface.

The mechanism of the adsorption of QAs and of the HUMIC material on acicular sodium oxalate in synthetic liquor is not clarified. Charged surfaces usually favour the adsorption of a species of opposite charge. Due to the very high ionic strength of liquor, the surface of sodium oxalate is presumably charged. It is still a question how both positively and negatively charged molecules can adsorb on the same surface.

It is difficult to interpret the results from a surface chemistry point of view. The surface charge of the oxalate crystal is un-known. All of the techniques used for determining the surface charge of crystals fail when the media is a Bayer liquor of high ionic strength and high pH. It is highly probable that in such a solution the electric double layer formed determines the adsorption behaviour of the surface and the original surface charge has less significance. The fact that both positively and negatively charged additives readily adsorb on the surface supports this hypothesis. The forms of surfactants or humates in which they exist in Bayer liquor is also un-known. The speciation study of Bayer liquor suggests that ions exist mainly as ion-pairs in Bayer liquor. The interactions of Bayer liquor species with surfactants or humates have not been clarified. More detailed discussion on surface interactions between the oxalate surface and quaternary amines or humates is not supported by the results presented in this work. Further investigations are needed to clarify the fine details of the surface chemistry of oxalate crystals in Bayer liquor.

A technique that is commonly used for imaging biological samples after treating the tissues with dyes, CLSM was employed to image plant humic material adsorbed on solid oxalate crystals. Humic material is a naturally fluorescent

substance. Neither sodium oxalate nor C18QA fluoresces under the confocal microscope. Solid acicular oxalate was conditioned in liquor containing HUMIC cake extract; and the humic material adsorbed on the oxalate surface was observed with CLSM. The HUMIC cake extract adsorbed all over the surface of the oxalate crystals including the end faces that were the main growing faces, but preferentially occupied the edges and corners of the crystals. The adsorption was not even: patches of humic material formed on the surface. The intensity of fluorescence increased after conditioning of the crystals in a mixture of HUMIC cake extract and C18QA. This indicated that significantly more humic material adsorbed on the crystal surface from the mixture. This result was consistent with that obtained using direct adsorption measurements.

In the presence of C18QA, humic material adsorbed on the main crystal faces as well as at the edges and in the corners. The growth rate of the main faces is slow and hence does not contribute much to the overall growth rate. That can explain why the excess humic material adsorbed with C18QA was less effective at inhibition than was expected given the amount of humic material adsorbed. The excess humic material did not adsorbed on the fast growing faces; most of it occupied crystal faces that did not contribute much to the overall growth rate.

Humic material of cake extract adsorbed on blocky sodium oxalate as well. Unfortunately, there are no crystallization results to compare the quantitative data to the images. No obvious difference was seen in the presence of C18QA.

It was interesting that the nucleation of oxalate from liquor containing HUMIC cake extract resulted in crystals with a different morphology. Ball-like crystals, "poppy seed" crystals were formed. It could be observed with the confocal microscope that the humic material was incorporated in the crystal lattice. From a mixture of C18QA and HUMIC cake extract, doughnut-like crystals with a hole in the middle of the crystals were formed. The formation of "poppy seed" occurs under plant conditions. However, the exact conditions are not known, and very little of the crystal structure of this humate-sodium oxalate crystal form is known.

The adsorption of C12QA, C14QA and C16QA on sodium oxalate has been already investigated by FTIR-ATR (Hind, Bhargava & Grocott 1997b). Now, FTIR measurements were performed to investigate the nature of the adsorption of C18QA on solid oxalate from synthetic liquor. The secondary aim of the measurements was to develop a technique suitable for FTIR measurements of C18QA adsorbed on the

solid/liquid interface in synthetic liquor. In good agreement with previous results, FTIR detected the adsorption of C18QA on solid oxalate. The adsorption of HUMIC cake extract was seen as well. The characteristic peaks for humic material and C18QA appeared at the same wave numbers, corresponding to the asymmetric and symmetric CH_2 stretching vibrations of a methylene chain.

In summary, this project revealed that QAs do not play a direct role in the inhibition of crystal growth of sodium oxalate. Although QAs adsorb on the surface of sodium oxalate, they do not inhibit crystallization. Other organics are necessary to promote the inhibitory effect, therefore, stabilize the liquor. Plant humates were found to be very effective in this role. Many chemicals were tested and shown to exhibit behaviours that were similar to the effect of plant humates.

The role of QAs is to interact with plant organics and to promote excess organics to adsorb on the oxalate surface. The amount of excess humics is proportional to the QA concentration. As QAs increase, the amount of plant humates adsorbed onto sites that block crystal growth (end faces and step edges) also increases, resulting in an enhanced inhibition of crystal growth. It was shown, however, on the CLSM images, that much humic material is adsorbed onto sites on the oxalate crystals that do not block crystal growth as efficiently (main faces) when adsorbed together with QAs. This can explain why the plant humates co-adsorbed with QAs show less effective inhibition than would be expected from the amount of plant humates adsorbed.

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