INTERFACIAL STUDIES IN THE ZINC PRESSURE LEACH TECHNOLOGY

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Abstract

Interfacial tension measurements in the liquid sulphur - zinc sulphate solution system, and contact angle measurements in the liquid sulphur, aqueous solution and zinc sulphide mineral were made at a temperature of $125 \pm 4°C$ under superatmospheric conditions using the pendant drop technique. The purpose of these measurements was to study the dramatic effect of surface active agents, particularly ligninsulphonate on the performance of the zinc pressure leach.

The measurements obtained showed that, in the absence of surfactant, the liquid sulphur - aqueous solution interfacial tension was 54 ± 1 dynes/cm and this value was reduced to 27–30 dynes/cm when 0.3g/l ligninsulphonate was present in the system. The contact angle obtained was $80\pm5°$ in surfactant-free system. This value increased to $148 \pm 5°$ when 0.3g/l ligninsulphonate was present in the system. The reduction in the interfacial tensions, combined with the mechanical agitation of the slurry disperses the liquid sulphur into small droplets in the slurry and the increase in contact angles reduces the liquid sulphur - solid mineral adhesive work from 63.7 ergs/cm^2 in the surfactant-free system to about 5.3 ergs/cm^2 in the presence of 0.3g/l ligninsulphonate. These properties enhance sulphur removal from the surface of any unreacted zinc sulphide mineral in the zinc pressure leach technology. These results indicate that the surfactant is adsorbed at both liquid sulphur - aqueous solution and aqueous solution - marmatite mineral interfaces.

Acknowledgement

Table of Contents

List of Tables

List of Figures

List of Symbols

R_1, R_2 – radii of curvature

p – differential pressure, atmospheres

γ – interfacial tension, dynes/cm

ρ – difference in density between liquids under test, kg/m^3 or g/cm^3

y – vertical height of liquid measured from apex of drop, cm or m

g – acceleration due to gravity, 9.81 m/s^2 or 981 cm/s^2

Y, Y', Y'' – dimensionless variables

β – dimensionless parameter

S – shape ratio of pendant drop

d_e – equatorial diameter of drop, cm

d_s – diameter of drop at a distance d_e from apex, cm

H – dimensional parameter as a function of drop shape

w_o – original diameter of drop forming tip, cm

w_m – magnified diameter of drop forming tip, cm

d_e^m – magnifeid diameter of pendant drop, cm

θ – mineral - liquid sulphur contact angle

γ_{MA} – mineral - aqueous solution interfacial tension, dynes/cm

γ_{SA} – liquid sulphur - aqueous solution interfacial tension, dynes/cm

γ_{MS} – mineral - liquid sulphur interfacial tension, dynes/cm

a – surface area of solid substrate in contact with liquid, cm^2

$-\Delta G_w$ –   surface free energy change, joules

W_a –   reversible work of adhesion per unit area, joules/cm^2

t –   time in minutes

κ –   curvature of a curve

ϕ –   inclination of a tangent to the curve at point P(x,y)

σ –   radius of curvature

$x, y,$ –   dimensions of a two dimensional space

Chapter 1

INTRODUCTION

About 80 % of the worlds primary zinc production is derived from sphalerite(ZnS). Coventionally, the ZnS concentrate undergoes a preliminary roast to convert the sulphide into zinc oxide at about $950 - 980°C$. The roasting process produces SO_2 as a major by-product along with dusts and fumes containing over 30 elements. The sulphur dioxide is then converted into sulphuric acid in an acid plant which in most cases is also erected as part of the zinc plant. The ZnO produced in the roast is then leached in a dilute sulphuric acid solution in order to solubilize a maximum amount of zinc, and other metals, such as cadmium, and copper, and at the same time eliminate most impurities. The pregnant solution is then purified and subjected to electrolysis to electrowin the zinc. Thus, any expansion to the zinc plant requires extensive increases in acid production, in roaster capacity, and in the electrowining tank rooms.

Since the cost of recovering SO_2, converting it into acid, and shipping it to market almost always exceeds the market value of the acid, and since even high SO_2 concentrations lead to an atmospheric pollution problem, the zinc pressure leach technology has certain potential advantages over the conventional roast-leach technology. It offers dissolution of zinc from the concentrate with high zinc extraction (about 96 to 98 %) and the production of elemental sulphur(more than 87 %) without any sulphur dioxide produced.

1

The zinc pressure leach has been known as far back as 1954, when Bjorling [1] mentioned the reaction:

$$ZnS + H_2SO_4 + 1/2O_2 \longrightarrow ZnSO_4 + S^\circ + H_2O \qquad (1.1)$$
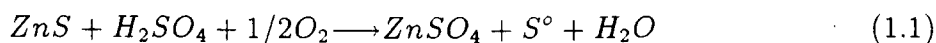
as having been carried out using oxygen under pressure, but pointed out that this reaction proceeds so very slowly such that it is impractical for zinc extraction from zinc sulphide unless nitric acid is also present as a promoter. However, during the subsequent electrolysis, the nitric acid prevents zinc plating, thus making the process economically unviable. In 1957, F.A. Forward and H. Veltman [2] improved upon Bjorling's results by repeating the experiment in a solution containing sufficient sulphuric acid to combine stoichiometrically with zinc in the zinc sulphide without nitric acid being present. They found that when the reaction was carried out at 140°C, the process ceased completely in about 10 minutes giving 65-72 % zinc dissolution. Further leaching of concentrate for up to 6 hours at 140°C affected only minor increase in dissolved zinc. This low extraction rate was due to molten sulphur occluding the unoxidized zinc sulphide particles. Although complicated methods for recovering the unleached zinc sulphide and recycling it to the process were developed, this problem continued to 'haunt' the process for the next twenty years. Finally a solution was found to the sulphur problem - the introduction of a suitable surface-active agent into the system during the pressure leaching. The surface active agent dispersed the liquid sulphur that previously inhibited high zinc extraction, and so made it possible to commercialize the process.

The pressure leaching of zinc sulphide concentrate is carried out using oxygen as an oxidizing agent. The whole process as currently practiced takes place at temperatures between 135 and 155°C, and at a total pressure of around 14 atmospheres. The overall reaction of the oxidative pressure leaching of the zinc sulphide concentrate is represented as:

$$ZnS + H_2SO_4 + 1/2O_2 \longrightarrow ZnSO_4 + S(l) + H_2O \tag{1.2}$$
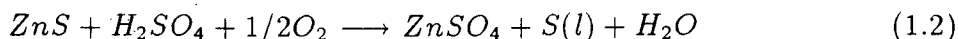
an exothermic reaction. This reaction is impractically slow in the absence of dissolved iron, which acts as a catalyst. The sequence of reactions including this iron catalysis can be represented by the equations:

a) gas-liquid mass transfer of oxygen

$$O_2(g) \longrightarrow O_2(aq) \tag{1.3}$$

b) homogeneous oxidation of ferrous ions

$$2Fe^{2+} + 1/2O_2(aq) + 2H^+ \longrightarrow 2Fe^{3+} + H_2O \tag{1.4}$$
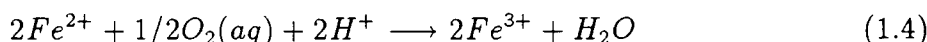
c) ferric ion leaching of zinc sulphide

$$2Fe^{3+} + ZnS \longrightarrow Zn^{2+} + S(l) + 2Fe^{2+} \tag{1.5}$$
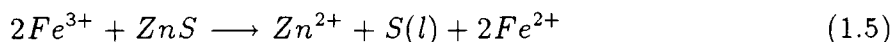
with cyclic regeneration of Fe^{3+} by reaction 1.4. Normally, there is sufficient acid-soluble iron in the concentrate(in the form of marmatite,(ZnFe)S, pyrite(FeS_2), pyrrhotite(FeS)) to satisfy the iron requirement for catalysis.

Hydrolysis reactions which occur alongside the leaching remove iron and lead from solution and result in the regeneration of some sulphuric acid:

$$3Fe_2(SO_4)_3 + 14H_2O \longrightarrow 2H_3OFe_3(SO_4)_2(OH)_6 + 5H_2SO_4 \tag{1.6}$$

$$3Fe_2(SO_4)_3 + PbSO_4 + 12H_2O \longrightarrow PbFe_6(SO_4)_4(OH)_{12} + 6H_2SO_4 \tag{1.7}$$
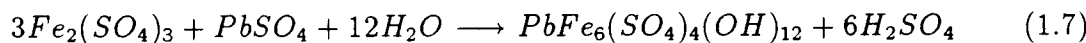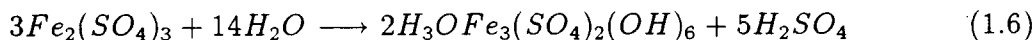
The operating temperatures exceed the melting point of the elemental sulphur produced in reaction 1.5. The molten sulphur then 'wets' the zinc sulphide particles (as

was observed by Forward and Veltman) and thus retards the progress of the process. To prevent the sulphur behaving this way, a surfactant - a salt of ligninsulphonic acid (marketed as lignosol) has been found which, when introduced into the system acts as a dispersant and prevents the zinc sulphide particles from being coated with the molten sulphur, thus enhancing the reaction. The use of temperatures below the melting point of sulphur in the leaching step eliminated the need for a sulphur dispersant. However it has the disadvantage that the retention time required to affect substantially complete extraction of zinc values is undesirably prolonged.

The mechanism by which ligninsulphonic acid prevents the molten sulphur from occluding the sulphide particles is by dispersing it in the solution in the same way as a domestic detergent disperses oil in water.

The melting point of sulphur could be either 113°C or 119°C depending on the crystalline allotrope. Below 94°C, sulphur exists as rhombic sulphur and above 94°C, it exists as monoclinic , figure 1.1. However, the transition from rhombic to monoclinic is slow and if the rhombic form is heated rapidly, it can easily reach its melting point-113°C and spread before recrystallizing to the monoclinic form (melting point-119°C). Thus, it is easy for the sulphur produced in the process to be molten, wetting the mineral and impeding the leaching reaction (without lignosol).

The behaviour of the lignosol and its role in the leaching kinetics in the system has been the subject of very few investigations. It is the object of this thesis to study the behaviour of the surfactant in the liquid sulphur- zinc sulphide-aqueous phase system.

With the introduction of the surfactant, the surface and interfacial tensions of these phases may or may not be affected. The interfaces present in the system are:

1. aqueous solution - gas interface

2. solid - aqueous solution interface
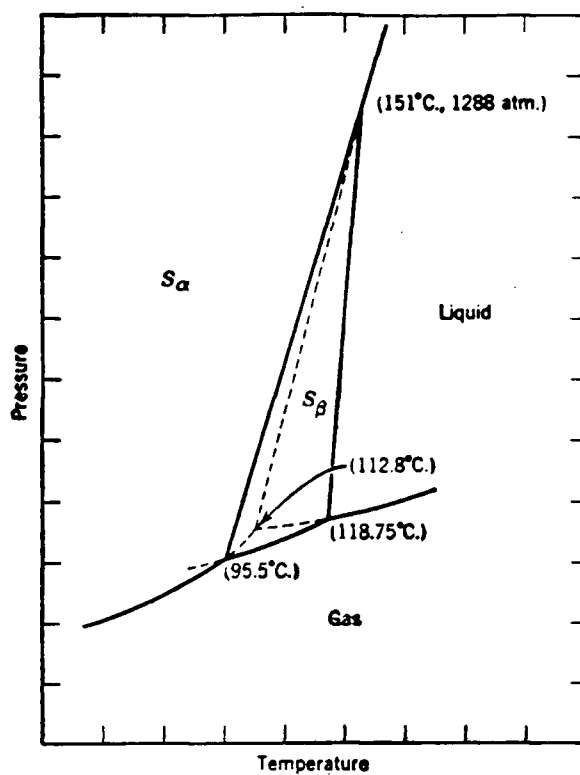
Figure 1.1: Sulphur Phase Diagram

3. solid - gas interface

4. sulphur - aqueous solution interface

5. sulphur - gas interface

6. sulphur - solid interface

With the exception of any solid - liquid interfaces, these interfacial tensions are measurable within the limits of available experimental techniques.

Chapter 2

LITERATURE SURVEY

Available literature indicates that there have been no direct investigations into the interfacial phenomena involved in the zinc pressure leaching technology, (particularly the role of the detergent at temperatures between $120 - 150°C$ that characterize the modern zinc pressure leach) although studies have been conducted in other unrelated areas like benzene-water, heptane-water, mercury-water, etc. The only information available is that in the presence of ligninsulphonate, liquid sulphur does not completely 'wet' the zinc sulphide particles and hence the efficiency of the pressure leach process is enhanced [3]–[10]. However, the effects of such parameters as oxygen partial pressure, temperature, percent solids, agitation, sample size, foreign ions(heavy metal ions such as Fe^{2+}, Fe^{3+}, Cu^{2+}, Co^{2+}, Ni^{2+} etc.), sulphuric acid concentration, lignosol concentration etc. have been the subject of many investigations.

Xia Guang- Xiang et al. [3] concluded from their studies on the physical chemistry of the acid pressure leaching of zinc sulphide concentrates that in the absence of lignosol, the sulphide particles were 'wetted' by molten sulphur produced during the course of the reaction(reaction was carried out at $150°C$) and this resulted in only 50 % zinc extraction. However, in the presence of lignosol the rate increased until a constant rate value was obtained beyond which any further increase in the lignosol concentration had no noticeable effect. The source of the surfactant was noted to be unimportant provided the amount of the effective ligninsulphonate in the slurry is the same.

Recent work by Dreisinger et al. [4] supports the above observations. They observed

that the rate of the chemical reaction increased with increasing lignosol concentration up to about $0.05 g/l$ beyond which any further increase had no effect on the rate. They observed further that the surfactant degrades rapidly under pressure leaching conditions. Haung and Bernal [9] arrived at the same conclusions, based on an independent study.

2.1 INTERFACIAL PHENOMENA

An *interface* is the boundary between two adjacent bulk phases. When one of the phases is a gas or vapour, the term *surface* is used instead. An interface may be considered from a thermodynamic standpoint, either as a mathematical surface or as a distinct phase having a finite thickness. The properties(eg. density, composition, etc.) and energy characteristics of the material at an interface differ from that of the bulk phases on either side of the interface.

In multicomponent systems, composition in the interfacial region can differ dramatically from that of either bulk phase. This difference becomes very pronounced when surface-active materials or surfactants are present. These substances find it energetically favourable to be concentrated at the interface and depleted in the bulk phases. These surfactants produce a significant decrease in the interfacial tensions and alter wetting properties as well [11,12]. (Only a reagent that destroys a surface active agent can lead to an increase in surface tension).[1]

Interfaces are classified in terms of the three states of matter as follows:

1. liquid–liquid interface

2. solid–liquid interface

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[1]Surface tension (dynes/cm) has the same dimensions and is identified with surface free energy (ergs/cm^2). As a free energy, it will always decrease if a surface active agent spontaneously accumulates on the interface.

3. solid–gas interface

4. liquid–gas interface

Just as in bulk, the surface or interface material may exist in the solid, liquid, and gaseous states [13]. The boundary between phases is *not* necessarily a surface of discontinuity where properties (eg. density, composition, etc.) change abruptly but may be a region of a finite thickness where the change is gradual or continuous. In general, the properties of an interface between two phases will be affected by changes in either of the two phases involved.

The terms *lyophilic* (liquid-loving) and *lyophobic* (liquid-hating) are used to describe the tendency of a surface or functional group to become wetted or solvated. If the liquid medium is aqueous the terms *hydrophilic* and *hydrophobic* are used. Lyophilic surfaces can be made lyophobic, and vice versa by appropriate surface active agent (surfactant). The molecules of surface-active materials have a strong affinity for interfaces, because they contain both hydrophilic and lyophilic (oil-loving) regions [14].

Surface and Interfacial Tensions

Surface tension is the boundary tension between a liquid and a gas or vapour, and interfacial tension is the boundary tension at a phase boundary between two completely immiscible condensed phases. Nearly all of the common specific properties of fluids, such as density, boiling and freezing points, optical activity and thermal conductivity are properties of the main body of the fluid. The boundary tension is the best known property of liquid surfaces or interfaces.

The surface or interfacial tension is a measure of the free energy of the fluid interface. At equilibrium, the surface tension is the same at every point and in all directions *along*

the surface of the liquid.[2] Fundamentally, for a plane surface, the surface tension of a liquid is often defined as *force acting at right angles to any line of unit length* on the liquid surface. For a curved surface, the definition, while similar is slightly more complex. The more satisfactory definition of surface tension (or specific excess surface free energy) is *the work required to increase the area of a surface isothermally and reversibly by a unit amount.* The two definitions are dimensionally the same. For solids, it is convenient to define surface tension as the restoring force necessary to bring freshly exposed surface molecules to equilibrium position. The units of surface or interfacial tensions are *dynes/cm* (cgs units), *milli-Newtons/m (SI units).* The surface free energy is quantitatively the same, but has the units of $ergs/cm^2$ or $joules/m^2$ (in SI units).

At the interface between two liquids there is an imbalance of intermolecular forces. Interfacial tensions usually lie between the individual surface tensions of the two liquids in question. The tensions at the liquid-solid interface are also of importance, but cannot be measured as directly.

Surface Tension and Temperature

The surface tension of most liquids generally decreases with increasing temperature in a nearly linear relation (however, some metal melts eg. cadmium, iron, copper are exceptional in this respect, and there is no explanation for these abnormalities) and becomes very small in the region of the critical temperature, when the intermolecular cohesive forces approach zero. A number of empirical equations have been suggested by the various writers which relate surface tension and temperature (for pure liquids), the most notably being that of Ramsay and Shields [14]:

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[2]There are solid-solid interfacial tensions but they can't be measured. Solid-liquid interfaces also have interfacial tensions, which are very hard to measure but may be inferred from contact angle measurements.

$$\gamma \left(\frac{Mx}{\rho}\right)^{2/3} = k(T_c - T - 6) \tag{2.8}$$

- M is the molar mass of the liquid

- ρ is the density of the liquid

- x is the degree of association

- T_c is the critical temperature

- k is a constant

Ramsay and Shields assigned a k value of 2.1 for a number of normal substances eg. carbon disulphide, carbon tetrachloride, ethyl ether, benzene, chlorobenzene, ethyl acetate etc. , however, for certain liquids like water, alcohols, and carboxylic acids, Ramsay and Shields found that the constant k (ie. temperature coefficient) was less than 2.1 and also varied with temperature. They attributed this to the fact that these substances are associated in the liquid state.

Boundary Tension and Pressure

Massoudi et al. [15] investigated the effect of hydrostatic pressure on the surface tension of aqueous solutions such as NaCl, and tetra-n-butylammonium bromide under atmospheres of compressed gases at 25°C using the capillary rise and maximum bubble pressure methods. The authors studied NaCl under atmospheres of CH_4, C_2H_4, C_2H_6, n–C_4H_{10}, and CO_2, and solutions of tetra-n-butylammonium bromide under the above atmospheric conditions as well as C_3H_8 and N_2O. Massoudi and co-workers observed that in the case of NaCl solutions, the change in surface tension with pressure was nearly independent of salt concentration, whereas for the tetra-n-butylammonium bromide, the

change in surface tension with pressure is sensitive to electrolyte concentration - at a given pressure, the surface tension decreases with increasing concentration. With NaCl solutions, all gases studied exhibit the same behaviour, whereas with the tetra-n-butyl solutions the effects produced by the gases differ depending on the nature of the gas, but at a tetra-n-butyl concentration in excess of 0.1m the electrolyte concentration ceases to have any effect on the sensitivity of surface tension to gas pressure.

R. R. Harvey [16] investigated the effect of pressure on the interfacial tension of the benzene-water system using the pendant drop technique at pressures of 68–1360 atmospheres and temperatures up to 100°C. He realised that interfacial tension values varied only 2–3 dynes/cm over the entire pressure range investigated and that the interfacial tension of the benzene-water system decreases only slightly with increasing pressure and shows slight though definite increases at low temperatures over the low pressure ranges.

Jho and King [17] studied the effect of pressure on the interfacial tension of n-hexane with water and aqueous solutions of sodium dodecyl sulphonate under pressures of dimethyl ether. Pressure is found to cause both positive and negative changes in interfacial tension depending on the system studied. Jho and King observed also that the pressure induced change of the interfacial tension between two condensed phases is usually much smaller than that found for a gas-liquid interface. They observed that the interfacial tensions were very sensitive to the presence of dissolved dimethyl ether. They concluded that the changes in the interfacial tension between hexane and aqueous solutions of sodium dodecyl sulphonate induced by dimethyl ether dissolved under pressure closely resemble results obtained in measurements involving the gas-aqueous solution interface. In the absence of surfactant, the authors conclude that the adsorption of dimethyl ether at low pressures is found to be approximately the same at both oil-water and gas-water interfaces. With surfactant (sodium dodecyl sulphonate) present, the pressure-induced changes in interfacial tension and adsorption isotherms indicate

that surfactant anions and dissolved ether molecules compete for available surface at the oil-water interface.

Hauser et al. [18] investigated the influence of pressure and temperature on the interfacial tension using the pendant drop technique operating in a pressure range of 1–700 atmospheres and temperature range of 20–200°C. The systems studied were benzene-water and n-decane-water. It was found that for benzene-water systems, the interfacial tension rose *only slightly* with pressure (in the range investigated) at 23°C but that at higher temperatures, the interfacial tension decreased with pressure. On the other hand, the n-decane-water system behaves differently. At room temperature the tension first rose by about 1.5 % up to a pressure of 350 atmospheres; at higher pressures the tension dropped off, so that at 700 atmospheres its value is about 1.3 % lower than that at atmospheric pressure. In both systems, the interfacial tension decreases with increasing temperature along an isobar (this has been established by many investigators), the rate of decrease being greater at higher temperatures. This rapid decrease is attributed to the mutual solubilities of the hydrocarbon and the water.

Effect of Dissolved Electrolytes on Boundary Tension

The effect of dissolved electrolytes on the surface or interfacial tensions could be a negative or positive contribution depending on the system under study and the concentration of the electrolyte.

Eversole and Dedrick [19] observed that the interfacial tension of mineral oil-sodium acetate systems decreases hyperbolically with increasing sodium acetate concentration from 0 to 6 molal. However, sodium formate was found to behave differently under similar experimental conditions. A plot of the interfacial tension–sodium formate concentration shows that the interfacial tension passes through a distinct minimum. At high

concentration of sodium formate the interfacial tension is greater than at zero concentration [19]. A sodium formate - toluene system behaves in the same way as mineral oil - sodium formate system. Against toluene, sodium acetate solutions yielded an interfacial tension curve which passes through a very abrupt minimum. The authors tried to explain this observation by basing their argument on electrical forces acting between ions in the interface. These forces act such that the acetate ions become concentrated in the interface, the hydrocarbon end pointing in the direction of the oil phase and the carboxyl group turning toward the water phase; decreasing the concentration of the salt in the water phase increases the attraction of the water phase for the carboxyl group and shifts the equilibrium position toward the water-like side of the interfacial layer; on the other hand, increasing the concentration of salt decreases the attraction of the water phase for the carboxyl end of the ion, and shifts the equilibrium toward the oil-like side of the interface. Benzene-water systems behave in a similar but slightly different form [20] - at very low concentrations, the interfacial tension of benzene-sodium acetate systems decreases markedly with increasing concentration of the salt up to about 0.1 molal, beyond which the interfacial tension increases quite abruptly with a small increase in concentration. It passes through a maximum then decreases hyperbolically as the solution approaches saturation. The authors concluded their findings as: any solute which is a strong electrolyte will cause an initial lowering of interfacial tension (when dissolved in water) and subsequent increase at higher concentration provided one ion has a greater tendency than the other to leave the aqueous phase and go into the non-aqueous phase. After the initial decrease and subsequent increase in the boundary tension, the effect of strong electrolytes at still higher concentrations depend on the tendency of the electrolyte as a whole to pass through the interfacial layer into the non-aqueous phase as doublets or undissociated molecules.

2.2 CHARACTERISTIC FEATURES OF SURFACTANTS

A surface-active agent (or surfactant) is a substance that, when present at low concentration in a system, has the property of adsorbing onto the surfaces or interfaces of the system and of lowering to a marked degree the surface or interfacial free energies of those surfaces or interfaces. Surfactants always act to reduce interfacial free energy rather than to increase it although there are occasions when they are apparently used to increase it [21].[3] Surfactants become significant (or applicable) when the interfacial phenomena occuring at phase boundaries within a system are so unusual relative to the expected bulk phase interactions that the entire system behaviour becomes dependent on the interfacial process (eg. corrosion, detergency or flotation).

Surfactants have characteristic molecular structure consisting of a structural group that has very little attraction for the solvent, known as a lyphobic group, together with a group that has strong attraction for the solvent, called lyophilic group. This is known as *amphipatic* structure. In solution, the presence of the lyophobic group in the interior of the solvent causes a distortion of the solvent liquid structure, increasing the free energy of the system. In an aqueous solution of a surfactant, this distortion of the water by the lyophobic (hydrophobic) group of the surfactant and the resulting increase in the free energy of the system when it is dissolved means that less work is needed to bring a surfactant molecule than a water molecule to the surface. The surfactant therefore concentrates at the surface. This decreases the surface/interfacial tensions. On the other hand, the presence of the lyophilic (hydrophilic) group prevents the surfactant from being expelled completely from the aqueous phase. Thus, the amphipatic structure causes the reduction of the surface or interfacial tension of the solvent as well as orientation of the

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[3]Because surface tension is a free energy, a 'surfactant' that raises the surface/interfacial tension must necessarily interact with, and reduce the adsorption of a previously present (though not necessarily detectable) surfactant.

molecules at the surface or interface with its hydrophilic group in the aqueous phase and its hydrophobic group oriented away from it.

The chemical structure of groupings suitable as the lyophobic and lyophilic portions of the surfactant molecule vary with the nature of the solvent and the conditions of use. As the temperature and use conditions (eg. presence of electrolyte or organic additives) vary, modifications in the structure of the surface-active agent becomes necessary. Thus, for surface activity in a particular system the surfactant molecule must have a chemical structure that is *amphipatic in that solvent under conditions of use.*

The hydrophobic group is usually a long chain hydrocarbon residue, less often a halogenated or oxygenated hydrocarbon; the hydrophilic group is an ionic or highly polar group. Depending on the nature of the hydrophilic group, surfactants are grouped as:

1. anionic - the surface-active portion of the molecule has a negative charge e. g. ligninsulphonates, xanthates, and carboxylates.

2. cationic - the surface-active portion bears a positive charge e. g. $RN(CH_3)_3^+ Cl^-$ (quarternary ammonium chloride).

3. zwitterionic - both positive and negative charges may be present in the active portion e. g. amino acids such as glycine.

4. nonionic - the active portion bears no apparent ionic charge e. g. tergitol (a derivative of ethylene oxide).

The choice of a particular surfactant depends on availability, cost and efficiency; the most inexpensive and efficient surfactant is usually chosen for a particular purpose. This requires knowledge of : a) characteristic features of available surfactants (physical and chemical properties and uses), b) interfacial phenomena involved in the job to be done

and the role of the surfactant c) the surface chemical properties of various structural types of surfactants and the relationship of the structure of a surfactant to its behaviour in various interfacial phenomena [12,21,22].

In comparing the performance of different surfactants, it is necessary to distinguish between the *amount* of surfactant required to produce a given amount of change in the phenomena under investigation and the *maximum change* in the phenomena that the surfactant can produce, regardless of amount used. The former parameter is known as the efficiency of the surfactant and the latter its effectiveness.

2.3 REDUCTION OF SURFACE AND INTERFACIAL TENSIONS BY SURFACTANTS

Reduction of surface or interfacial tensions depends on the direct replacement of solvent molecules at the interface by molecules of surfactant [21]. For a system of two immiscible liquids, the greater the similarity between them in structure or in the nature of their intermolecular forces, the greater the interaction between them and the smaller the resulting interfacial tension between the two phases. The two phases spontaneously merge to form a single liquid if the interfacial region (and hence tension) between them disappears.

If a surface-active agent is added to two immiscible phases (a polar and a non-polar liquid), the surfactant gets adsorbed at the interface between the two, and orients itself at the interface with the hydrophilic group directed toward the aqueous phase and the hydrophobic group toward the non-aqueous phase. Where the surfactant molecules replace the aqueous molecules and the non-aqueous molecules of the original interface, the interaction across the interface will be between the hydrophilic group of the surfactant and the aqueous molecules on one side of the interface and between the hydrophobic group

and the non-aqueous phase on the other side of the interface. These interactions are much greater than the original interface interactions thus resulting in significant reduction in the interfacial tension by the presence of the surfactants. The lyophobic portion of the surfactant has two functions: a) to produce spontaneous adsorption of surfactant molecule at the interface and b) to increase the interaction across the interface between the adsorbed surfactant molecules there and the molecules in the adjacent phase. The function of the lyophilic group is to provide strong interaction between the molecules of the surfactant at the interface and the molecules of solvent. For any efficient surface activity, there should be a balance between the lyophilic and lyophobic characters in any given surfactant; this balance varies with the system and conditions of use.

2.4 PROPERTIES OF LIQUID SULPHUR

Sulphur is the element of atomic number 16, the second element in group VI of the periodic table and is non-metallic. At the melting point, sulphur forms a light yellow, low viscosity liquid. On heating, the liquid darkens, and becomes deep orange. With regards to the variation of viscosity with temperature, there are contradictions in literature. Whereas Nickless [23] reports that viscosity increases with temperature and passes through a maximum at 159°C, beyond which there is discontinuity in all physical properties, (this might be a mistake), Tuller and others [24]–[27], [29] report that the viscosity drops with increasing temperature up to about 159°C above which any further increase in temperature makes the liquid more viscous up to about 200°C beyond which it begins to fall again with increasing temperature, (see figure 2.2), such that at its boiling point of 444.60°C, it is again a mobile liquid. The increase in viscosity at temperatures above 159°C is assumed to result from rupturing of the puckered sulphur rings (S_8) to form chains of varying lengths. Above 200°C, the long chains begin to break up and the
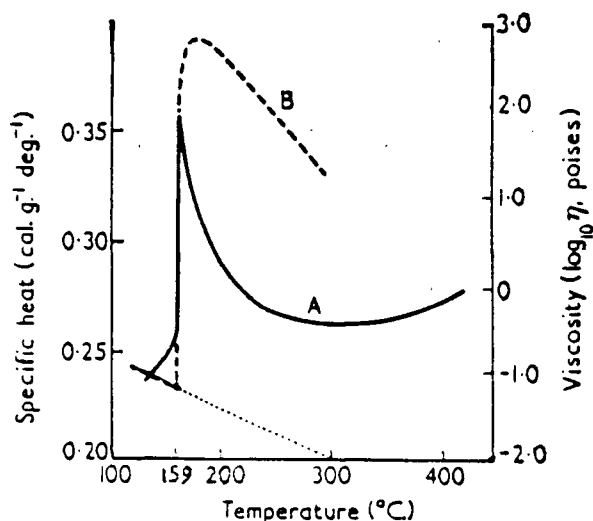
Figure 2.2: Viscosity of liquid sulphur

viscosity decreases with temperature.

The measurement of surface tension on highly purified sulphur was carried out by Fanelli [30]. He found that the surface tension decreases linearly with temperature, but that there is a sharp discontinuity at about 159°C, the rate of fall being smaller above this temperature. From Fanelli's results, an equation relating surface tension of sulphur to temperature was derived by Tuller [24]: below 159°C

$$\gamma = 73.4 - 0.105t \tag{2.9}$$

above 159°C

$$\gamma = 65.7 - 0.0566t \tag{2.10}$$

where t is the temperature in degree celcius, and γ is the surface tension in dynes/cm

The density of liquid sulphur has been reported as decreasing with increasing temperature. At 121°C, the value is 1.8037g/cm^3, at 124°C, the density is 1.8007g/cm^3, at 130°C the value is 1.7957g/cm^3, etc.

2.4.1 Allotropes of Sulphur

Solid sulphur has two main crystalline allotropes: - the rhombic (α) and monoclinic (β) allotropes. The rhombic allotrope is stable at STP up to about 95.4°C beyond which it slowly transforms to the monoclinic (β) type. Monoclinic (γ) sulphur is also reported to exist but its stability is still disputed. The melting points are 113°C, 119°C and 106.8°C respectively. Monoclinic (γ) sulphur transforms into monoclinic (β) and/or into rhombic (α) sulphur. Besides these crystalline or intermolecular allotropes the earlier literature reports molecular allotropes (eg. S_λ, S_π, S_μ) as well. Later investigators [23,25] report the molecular composition of liquid sulphur to be a mixture of S_8, S_x and S_4 molecules and their dynamic equilibria is dependent on the temperature history of the sulphur. Tuller [24] and Moeller [29] identified S_λ as having a structure and molecular weight equivalent to S_8 puckered rings; S_μ equivalent to S_x long sulphur chains and S_π equivalent to S_4 (being the most important of other molecular forms such as S_7, S_9,etc.). Tuller reports that at the melting point of sulphur, S_μ is practically nonexistent as an equilibrium component but that its concentration increases as the temperature increases beyond the melting point such that at the boiling point it constitutes 37 % of the equilibrium liquid. The molecular species, S_π, attains a maximum equilibrium concentration of 6.6 % at 200°C but then drops to 2.8 % at the melting point of sulphur and to 4 % at the boiling point. S_λ forms 97 % of equilibrium liquid at the melting point and this drops with increasing temperature to about 59 % at the boiling point; the decrease being compensated for by increase in S_μ. The 8-membered puckered rings and the long sulphur chains are in dynamic equilibrium. The equilibrium formula is:

$$x/8 S_{8(ring)} \rightleftharpoons S_{x(chain)}, where \ 0 < x < \infty \qquad (2.11)$$

Reports on gas phase studies indicate the presence of more than 10 % of S_6 and S_7 each in saturated vapour at 120°C, and it is reasonable to assume that they both occur

in the liquid phase.

2.5 LIGNINSULPHONATES/LIGNINSULPHONIC ACIDS

Ligninsulphonates are the products of digestion of liquified wood chips at temperatures of 125 - 145°C in an aqueous solution of sulphur dioxide and a salt of sulphurous acid, such as calcium bisulphite for a period of 8 - 24 hours (in the chemical pulping process), depending on the temperature and nature of pulp required. This process is known as *sulphonation*. Ligninsulphonates are derivatives of lignin whose exact definition and structure, Figure D.14, still remains a matter of debate,[4] thus the mechanism involved in the sulphonation of lignin to ligninsulphonates is also far from being understood [31].

2.5.1 Organic Chemistry

These compounds are complicated condensation polymers, fig. D.13, whose exact structure is not completely known. Ligninsulphonates or ligninsulphonic acids consist of polymeric condensation products of guaiacylpropane units (4-hydroxyl-3-methoxyphenyl) for the most part and less frequently 3, 5-dimethoxy-4-hydroxyphenylpropane and 4-hydroxyphenylpropane units, figure 2.3. The most common ligninsulphonic acids have a molecular weight of about 4000, however molecular weights can vary from 200 to 100,000. Sulphonate groups are attached to the carbon chains but not to the benzene ring. The sulphonatable carbon atoms are in Alpha-positions to the benzene ring. Secondary and tertiary OH^- groups are present in the side chains and these augment the hydrophilic properties of the ligninsulphonates provided by the sulphonic group.

Ligninsulphonic acids are only soluble in water or in a solvent where the *hydrogen bond* is very strong. They undergo hydrolysis or oxidation. Ligninsulphonates are anionic

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[4]Freudenberg was one of the pioneers of chemistry of lignin

i) 4-hydroxy-3-methoxyphenylpropane

OH — (benzene ring) — C — C — C —

OCH$_3$

ii) 3,5-dimethoxy-4-hydroxyphenylpropane

OCH$_3$

OH — (benzene ring) — C — C — C —

OCH$_3$
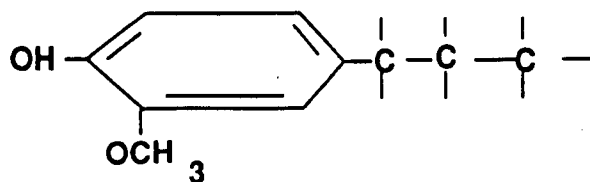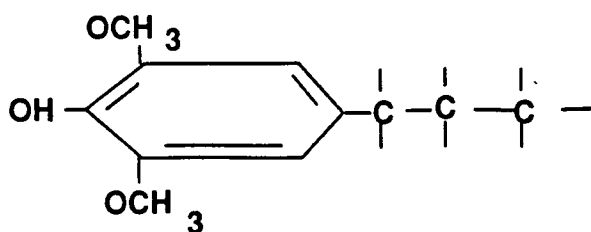
iii) 4-hydroxyphenylpropane

OH — (benzene ring) — C — C — C —
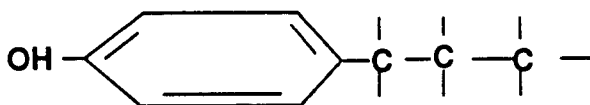
Figure 2.3: Monomeric (Basic) Structures of lignin

polyelectrolytes. The ligninsulphonate molecule is described as randomly coiled, cross-linked, polyaromatic chains with negatively charged sulphonate groups near the surface to maintain their solubility in water.

In general, lower molecular weight ligninsulphonates are more linear and associate in solution; higher molecular weight ligninsulphonates are more branched and exhibit polyelectrolyte behaviour in aqueous media [31,32,33].

2.5.2 Physical Chemistry

Ligninsulphonates/ligninsulphonic acids may be regarded as heterodisperse systems (in water solutions). They have a strong tendency to dissociate as well as associate and this makes the determination of molecular weight very difficult. Ligninsulphonic acids or the salts do not crystallise.

2.5.3 Adsorption Characteristics

The surface activity of ligninsulphonates is affected by the number of hydrogen bonding groups present in the molecule, such as side chain hydroxyl, phenolic and carboxyl groups. The adsorption of ligninsulphonates is known to be determined by the nature of hydrogen bonding. Ligninsulphonates do not form micelles. Ligninsulphonates sorb very poorly upon graphite surfaces which are known to be free of hydrogen bonding, but sorb quite well upon carbon blacks which are known to contain hydrogen bonds. *Ligninsulphonates are not capable of forming any oriented layer* when adsorbed upon a liquid or solid surface.

2.5.4 Interfacial Tension Characteristics

Ligninsulphonates, when in solution, concentrate only moderately at an air-water interface and are therefore capable of only mildly modifying the surface tension of water.

This compound (or reagent) requires about 5–6 % concentration to attain a maximum lowering of surface tension of about 45 dynes/cm. Surface tension reduction induced by ligninsulphonates exhibits considerable time-lag, with the most pronounced effects occuring in the first five minutes of aging [34].

The surface activity of ligninsulphonates is influenced by the presence of electrolytes in solution. In general, the more inhospitable the solvent, the greater will be the adsorption of ligninsulphonate at the interface [34].

Electrophoretic studies have shown that ligninsulphonates are strongly dissociated, even in 6 % solution [34].

2.5.5   Macromolecular Structure of Ligninsulphonates

The ability of ligninsulphonate to adsorb upon all kinds of surfaces susceptible to hydrogen bonding indicates the presence of available hydrogen bonding groups at the surface of the ligninsulphonate polyelectrolyte. The ligninsulphonates are insoluble in aliphatic and aromatic hydrocarbons. This property of the ligninsulphonates as well as their lack of pronounced surface and interfacial tension lowering (of organic compounds) indicates the absence of oil soluble groups in their structure.

The viscosity of solutions containing ligninsulphonates increases with concentration. This is also explained on the basis of hydrogen bonding groups present in their structure which cause increased interparticle attraction. The fewer these groups, or the lower the molecular weight, the less pronounced will be the viscosity-concentration effect.

Interparticle attraction among ligninsulphonate molecules are due to *Van der Waals and hydrogen bonding forces.* Thus, the stronger the electrokinetic force of repulsion between molecules, the lower will be the viscosity of the solution.

2.5.6 Correlation of Ligninsulphonate Structure with Surface-Active Properties

Ligninsulphonates are desorbed from clay surfaces in the absence of contaminating electrolytes by treating with sodium hydroxide to attain pH values in excess of 10 - this property of ligninsulphonates is employed in the treatment of aqueous drilling fluids. This results because the hydroxyl ion from the NaOH competes successfully with hydrogen bonding groups of the ligninsulphonate and thereby render them less effective as mud conditioning agents. On the other hand, if the concentration of the contaminating electrolyte is large enough to lower the solubility of the ligninsulphonate, addition of NaOH will increase its solubility and effectiveness [34].

Ligninsulphonates are capable of deffloculating suspensions of solids both by electrokinetic and multilayer stabilization. The deffloculation properties are improved by controlled contamination additions to the drilling mud. This technique has been used in lime-ligninsulphonate and gypsum-ligninsulphonate muds where both defflocculation of clay solids and filtration rates are improved by treating the mud with lime or gypsum.

Although electrolyte contamination can increase the effectiveness of ligninsulphonate-stabilised emulsion drilling fluids, the addition of a soap or surfactant with an oil-soluble group will adversely affect the ligninsulphonates. Such surfactants displace the ligninsulphonates from the oil-water interface, thus destroying the filtration control mechanism of the ligninsulphonate multilayer.

Increased multilayer adsorption of the ligninsulphonate can be induced by the addition of contaminating electrolytes to the drilling mud, or by synthesizing more hydrogen bonding groups in the ligninsulphonate molecule, and this will increase mutlilayer adsorption upon clay surfaces.

2.5.7 Modification of Ligninsulphonates

Any carbohydrate (these are of low molecular weight) present in spent sulphite liquor tend to contaminate the ligninsulphonate. The carbohydrates tend to compete with the ligninsulphonate for adsorption at reactive sites and, by blocking these sites render the ligninsulphonate less effective. Thus, any carbohydrate present should be effectively removed.

The electrokinetic properties of ligninsulphonates may be improved by increasing the degree of sulphonation. Enhanced adsorption characteristics and improved multilayer formation all may be induced by creating more hydrogen bonding groups in the molecule [31].

2.5.8 Other Properties

Ligninsulphonates/ligninsulphonic acids belong to the sulphonic acid group [35], hence, they possess some of the characteristics of sulphonic acids. Like all other sulphonic acids, ligninsulphonic acids (or ligninsulphonates) have characteristic polar properties. They are soluble in water (due to presence of hydrogen bonding) but not in any other organic solvent. They ionize (or dissociate) in solution according to:

$$R - \underset{\underset{SO_3H}{|}}{\overset{|}{C}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \; + H_2O \implies R - \underset{\underset{SO_3^-}{|}}{\overset{|}{C}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \; + H_3O^+ \qquad (2.12)$$
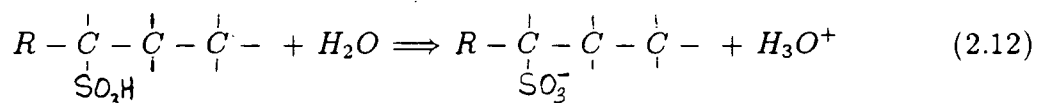
Ligninsulphonates behave as *anionic* surfactants - anionic surfactants are those which give negatively charged surfactant ions in aqueous solution:

$$R - \underset{\underset{SO_3Na}{|}}{\overset{|}{C}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \; \implies R - \underset{\underset{SO_3^-}{|}}{\overset{|}{C}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \; + Na^+ \qquad (2.13)$$
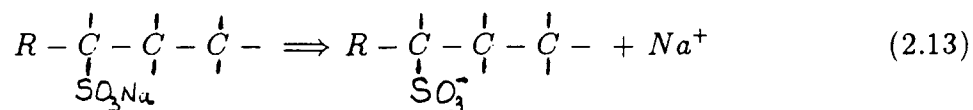
The negatively charged portion (i. e. anion) is the larger of the two ions and the active

cleaning agent. With sodium hydroxide, the reaction is:

$$R - \overset{|}{\underset{\underset{SO_3H}{|}}{C}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \; + \; NaOH \implies R - \overset{|}{\underset{\underset{SO_3Na}{|}}{C}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \; + \; H_2O \qquad (2.14)$$
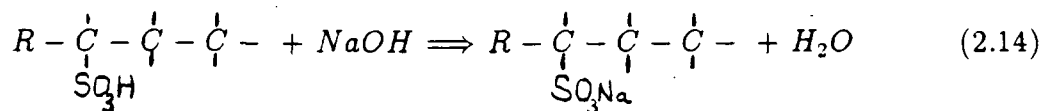
The dispersing effect is also apparently proportional to the number of electronegative groups such as chloro, hydroxyl, or nitro groups in lignin compounds of the same molecular weigh. However, there is no relationship between despersing effects and degree of sulphonation.

2.5.9 Uses and Applications of Ligninsulphonates

Uses based on Physical properties

The major quantity of purified ligninsulphonates is used in oil-well drilling mud formulations. The ligninsulphonates are effective in controlling the fluidity of the drilling mud, keeping inorganic earth and mineral salt contaminants encountered in drilling suspended and preventing them from flocculating the mud while, at the same time, performing a sequesting function. In the petroleum recovery process, an addition of a small amount of spent liquor solids to a commercial petroleum sulphonate results in a reduced interfacial tension. Tests also show that an addition of spent sulphite liquor solids having Na or NH_3 as a base increased oil recovery by up to 20 %. These increases are comparable in magnitude with those obtained using commercial ligninsulphonate products alone. When introduced as a surfactant, as much as 90 % reduction in interfacial tension over that observed with petroleum sulphonate is observed.

The second largest use of ligninsulphonates is in pelletizing animal feeds. This application does not require the purified grade. Ligninsulphonates play very important roles in the mining industry - they function as ore-flotation agents for a number of minerals.

They act as depressants for such minerals as calcite, barite, talc, sericite, molybden-ite, and carbonaceous materials such as graphite. They are also very good dispersing agents for slimes and are used for this purpose in both the flotation and tabling of slimy ores. In tabling operations, ligninsulphonates disperse the slime and prevent occlusion of ore particles. In flotation operations the dispersing action on slime increases the degree of separation, which results in an increased recovery and better grade of concentrate. They are also used to aid fluid pipeline transport of powdery ores [31,36,37]. A study of the flocculating properties of ligninsulphonates shows that low-molecular weight lignin-sulphonates acts as a dispersant at all concentrations (even in the presence of alum), high-molecular weight ligninsulphonate, in contrast, acts as flocculating agent at low concentrations and as dispersant at high concentrations. The flocculating rate increases with the molecular weight of the ligninsulphonate and is greatly enhanced by the presence of alum. Reducing the pH enhances the dispersing action of the low molecular weight ligninsulphonates. Hardwood ligninsulphonates are of too low a molecular weight and hence they exhibit poorer dispersant properties than softwood ligninsulphonate. Other uses of ligninsulphonates as effective dispersants are in the blending of carbon black into rubber, the distribution of vat dyes in the textile industry, the preparation of wettable agricultural powders and sprays, and the manufacture of portland cement - when added in small amounts to cement raw materials in the wet process. Ligninsulphonates are strongly adsorbed at the liquid-solid interface and reduce the viscosity to a point where much less water is required. This results in an increase in compressive strength of the cement. The purified ligninsulphonates can be used also in the ceramic industry for clay deflocculation; when added in small amounts, they increase the dry strength of ceramic bodies and improve plant efficiency.

When compounded with polyvinyl alcohol, they produce an excellent rewetting adhesive. Purified ligninsulphonates are also used in industrial cleaning compositions, particularly those meant for metal working.

Uses based on Chemical properties

They form insoluble protein complexes, and can thus be used to remove contaminating protein matter from canning-plant effluents, or as binding agents in impregnating paper bond with casein, and as an ingredient to aid in tanning of leather. Ligninsulphonates are good sequestrants for heavy metal ions such as ferric, cupric, and stannous, and (less effectively) for cobalt, manganese, nickel, silver, stannic, uranium, and zinc. They are also used in water treatment, as well as in agriculture. Ligninsulphonic acids and NH_4^+ ligninsulphonates undergo condensation reactions with phenyl-formaldehyde resins of various types to make low-cost binding and laminating resins [31,36].

Chapter 3

EXPERIMENTAL SET UP

3.0.10 Aims and Objectives of Investigation

The object of this investigation is to study the interfacial phenomena involved in the zinc pressure leaching technology. This includes investigations into the role of the lignin-sulphonate (surfactant) in the leaching kinetics of the process, especially with regards to its effect at the liquid sulphur - zinc sulphide mineral - aqueous phase system. The other area of interest is the source of the surfactant and its effect on the interfacial properties of the system.

The method chosen for this work involves the determination of liquid - liquid interfacial tensions and solid - liquid contact angles. There are numerous techniques for determining these quantities; however each of these techniques has its limitations. From references, [17,18,38,39,40], the method of pendant drops has a number of outstanding advantages over other methods. One of these is the fact that the method is a static one. Once the surface of the drop is formed, it is not subjected to any changes due to outside influence prior to or during the measurement. It is the only method which permits an accurate study of changes in surface or interfacial properties with time. It is suitable for measuring the interfacial tensions between two liquids.

The pendant drop technique, in brief, consists of suspending a small drop of one liquid (the denser liquid) from the end of a vertical cylindrical tube in a second liquid (the lighter liquid). The surface of the drop will be a surface of revolution whose shape and size can be determined by measurements made on a photographic image obtained with

a special camera built for this purpose. The interfacial tension between the two liquids
can be calculated from simple measurements made on a photograph of the hanging drop,
to be described later.

3.0.11 Apparatus

The equipment used for the work (shown in figure 3.4) consists essentially of : i) a light
source, L, for backlightening the drop ii) a stainless-steel bomb or thermstat, B, iii) two
or three sets of drop forming tips, V, iv) thermocouple v) a camera, C, for taking pictures
vi) rectangular optical glass cell(s), O.

Details of the equipment are shown in figure 3.4. The bomb is about 7.6cm in diameter
and 20.32cm high and consists of a drive-screw syringe, A, with a pyrex glass tubing tip,
V, for creating liquid sulphur drops (the tip is replaceable and the syringe can be opened
at both ends by means of screw caps) mounted on the outside of the chamber. It has
two 1.3cm sapphire windows, S, a thermowell, T, and a pressure gauge, H, for measuring
the pressure within the system at any time. The bomb is heated by wrapping it with a
heating tape followed by an insulating blanket. The inner chamber of the bomb must be
totally enclosed to prevent loss of liquid by evaporation. It is desirable that the tip be
made from tubing having a circular cross-section, and the end be cut off perpendicular
to a vertical axis. However, microscopic perfection is not essential since the liquid tends
to bridge over any minor irregularities.

3.0.12 Chemicals

The chemicals used are: reagent grade zinc sulphate salt, sulphuric acid, sulphur flowers,
ferric sulphate, ferrous sulphate, different salts of ligninsulphonate, zinc sulphide mineral
(marmatite) specimens obtained from Cominco Ltd. and pyrite specimens obtained from
the department collections(unknown source).
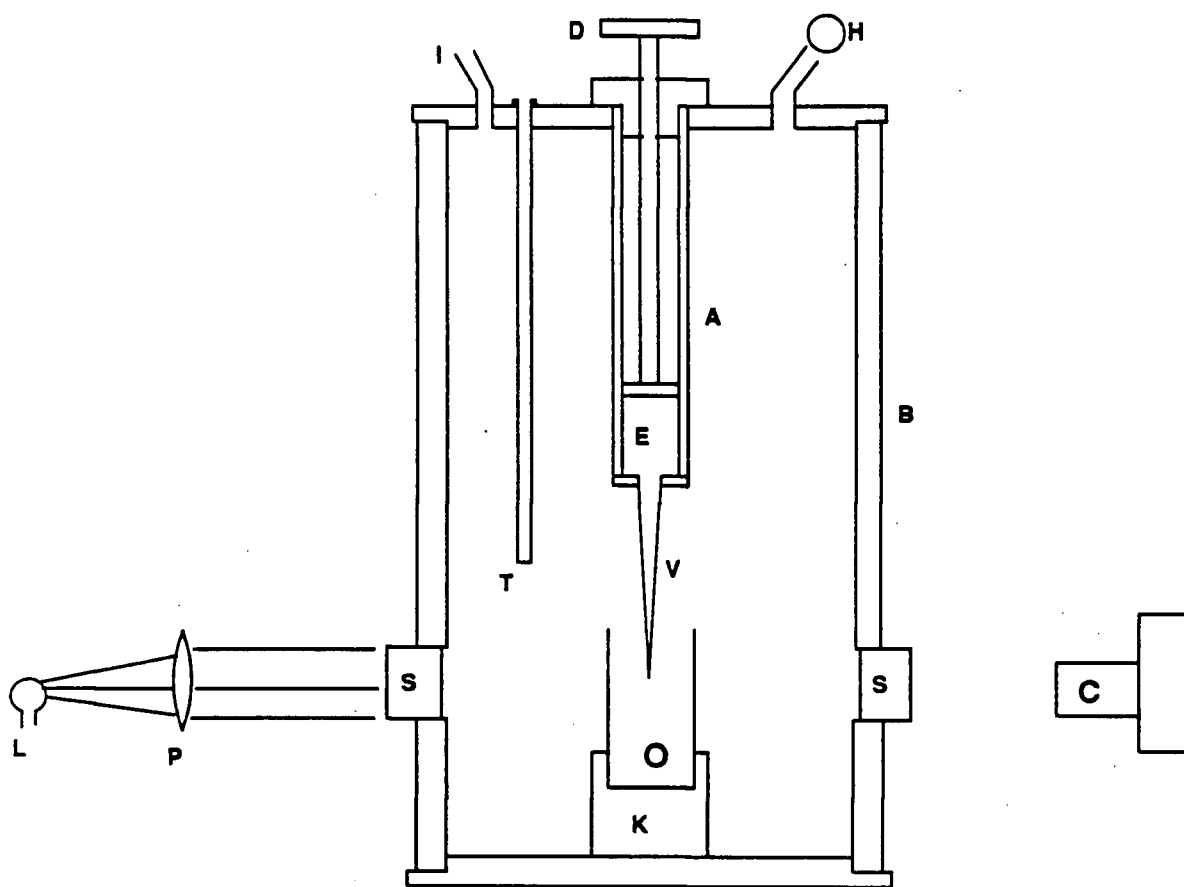
Figure 3.4: Cross section of high temperature and pressure stainless-steel bomb

3.0.13 Experimental Method

The equipment was carefully cleaned to get rid of any greasy material (or dirt) that might have come into contact with it during construction. A thermocouple was constructed from type E (chromel-constantan) wire and calibrated. The whole equipment was then calibrated for interfacial tensions using water and benzene at room temperature. After the interfacial tension calibration the equipment was thoroughly cleaned to make sure there is no residual benzene in the system to affect the subsequent determinations. The tests carried out include:

1. effect of pressure on aqueous solution-liquid sulphur interfacial tensions using nitrogen gas

2. effect of aqueous zinc sulphate concentration on the interfacial tensions

3. effect of sulphuric acid on aqueous solution-liquid sulphur interfacial tensions

4. effect of ferric and ferrous ions on the interfacial tensions

5. determination of contact angles between the mineral surface (marmatite or pyrite), liquid sulphur, and aqueous solutions

6. effect of ligninsulphonate concentration and its identification by source on the aqueous solution-liquid sulphur interfacial tensions and mineral-liquid sulphur contact angles.

With the exception of the first test, all experiments were carried out at $125 \pm 4^\circ$C and 80psi. Solutions used were sulphuric acid, pH=0.4, zinc sulphate solution varying in concentration from 0.1 to 2.0 molar, ferrous and ferric sulphate solution with Fe^{2+}=0.02 molar and Fe^{3+}=0.1 molar.

In all measurements of the aqueous solution-liquid sulphur interfacial tensions, the liquid sulphur is considered to be the denser of the two. For each experiment, the syringe is partially filled with sulphur. The rectangular optical cell was carefully mounted on an adjustable seat, K, in the bomb such that the sapphire windows of the pressure vessel were lined up with the optical sides of the cell. The cell was then carefully filled with the aqueous solution. The syringe was then mounted and the thermocouple inserted into the thermowell to record the temperatures as the bomb was being heated. The heating rate was controlled using a powerstat. The chamber was then closed and sealed and then subjected to nitrogen under appropriate pressure. At the melting point of sulphur ($\sim 120^{\circ}C$) the sulphur melted in the syringe. When the drive-screw of the syringe was moved in a downward direction the sulphur began to form pendant drops at the tip which was immersed in the aqueous solution. The position (i. e. height) of the tip was adjustable and this enabled the drop to be positioned appropriately to be photographed. Several drops were formed and photographed for each run after which one of the controlling variables was changed and the sequence of operations is repeated. It was essential for the drop to be photographed with rays of light which are parallel to the optical axis, if errors due to perspective were to be avoided. Measurements were made from the photographs. The measurements were made at points on the drop which were remote from the end of the tip and where the influence of imperfections in the shape of the tip is normally negligible. The interfacial tensions were calculated from the photographs of drop profiles. Adequate precautions were taken to ensure attainment of interfacial equilibrium. The required dimensions were measured with a rule graduated to 0.5mm. These dimensions were estimated to the nearest 0.1mm. Repeated measurements of the same drop is reproducible to within ±0.1mm.

The magnification of the pendant drop was determined from a knowledge of the enlarged diameter of the capillary tip, whose actual diameter was known to within

±0.002mm.

The first sets of experiments performed were with sulphur and zinc sulphate solution only, in which the effect of pressure on the aqueous solution- liquid sulphur interfacial tensions was tested. The pressure was varied from 40psi to 90psi for a given concentration of the solution. This was followed by the effect of solution concentration in which the concentration was varied from 0.1 to 2.0m and then the effect of ligninsulphonate and its concentration (concentration varied from 0.06-0.5g/l) on the interfacial tensions.

The second sets of experiments were to determine the effects of: a) sulphuric acid, pH=0.4, b) acid and the presence of iron (in the form of Fe^{3+} and Fe^{2+}, pH=0.4) on the zinc sulphate - liquid sulphur interfacial tensions. In this test both the zinc sulphate salt (at 1.5m concentration) and Fe^{3+}/Fe^{2+} were separately dissolved in sulphuric acid (pH=0.4) to keep the iron in solution at high temperatures since it is known that the tendency for Fe^{3+} to hydrolyse increases with temperature and pH. Tests were carried out with the zinc sulphate - sulphuric acid solution after which the sequence was repeated with the same solution composition but contains some few millilitres of Fe^{3+}/Fe^{2+}. After this, 0.3g/l ligninsulphonate was then introduced to determine how it affects the interfacial tensions in the presence of acid with and without iron (conditions which characterise the zinc pressure leaching). Dreisinger et al. [4] have observed that under the pressure leaching conditions the surfactant degrades with a half life of about ten minutes, so certain precautions were taken to ensure that the surfactant remains 'alive' at least in the time space during which the drops are being photographed. These precautions demand that the bomb be modified to take up a second drive-screw syringe. Thus, the Fe^{3+}/Fe^{2+} solution was held in the second syringe during the heating time to about 118-120°C after which some few drops were injected into the optical cell which contains the zinc sulphate - sulphuric acid -ligninsulphonate solution. All experiments were done in duplicates and some in triplicates to ensure that any data obtained were reproducible.

The last sets of tests were the determination of sulphide mineral - liquid sulphur contact angles. The minerals used were marmatite and pyrite and the determinations were carried out separately in the following enviroments:

1. zinc sulphate (1.5molar) solution, with and without ligninsulphonate (0.3g/l)

2. acidified zinc sulphate solution

3. acidified zinc sulphate solution and Fe^{3+}/Fe^{2+} with and without surfactant (0.3g/l)

The technique employed here was basically the same as the previous tests. The only difference here was that a picture is taken of liquid sulphur resting on a solid mineral (marmatite or pyrite) surface in an aqueous enviroment. The mineral was carefully mounted in the optical cell to be as horizontal as possible and the drops were controlled to be able to determine both the receding and advancing contact angles. After each run, the mineral was carefully cleaned to remove any residue that might have been deposited on the surface during the course of the experiment. These angles were measured directly from the photographs. However, obtaining a valid reproducible value was found to be complicated and difficult for a number of good reasons:

1. contamination of the sulphur drop by adsorption of impurities from the aqueous phase tends to reduce the angle

2. a solid surface, even when apparently smooth may have impurities and defects that vary from place to place on the surface and from sample to sample

3. the contact angle may show hysteresis. Contact angle hysteresis is always present especially when the surface is not clean, when it contains some amount of impurities, or when it is not perfectly polished.

These tests were repeated for three different salts of ligninsulphonate to determine the effect of the origin of the surfactant on the interfacial tensions. The role of quebracho, a suggested organic additive in the zinc pressure leaching is also investigated. Some investigators introduce this organic material as an additive supplementary or replacing the ligninsulphonate in the pressure leaching operations, but the material has been used only for empirical testing.

Chapter 4

THEORY and CALCULATIONS

4.1 Interfacial Tensions

Whereas the contact angles can be measured directly from the photographs, the interfacial tensions have to be computed using mathematical techniques available in the literature [17,18,38,39,40]. Two techniques are available for the mathematical treatment of the pendant drop profile: a) the method of the plane of inflection and b) the method of a selected plane. However, the method of the plane of inflection has two severe limitations which make its application very tedious and inaccurate. These are i) it is necessary to locate the true plane of inflection (which is graphically difficult) since a slight deviation from the true plane might introduce a large error and ii) it is necessary to compute the volume of the drop from its profile. These difficulties limit the precision of the method.

The second treatment is less direct and leads to more rapid and precise solution. This method consists of a careful consideration of the drop profile which is shown in figure 4.5. The profile is assumed to be at equilibrium with its surroundings, symmetrical and possesses two radii of curvature, R_1 and R_2 (as with any curved surface). At the apex (or bottom of the drop), O, the two are the same. The mathematical treatment is based on the assumption that the pressure difference developed at any curved surface due to the surface or interfacial tensions is proportional to the sum of the principal curvatures of the surface, i. e.
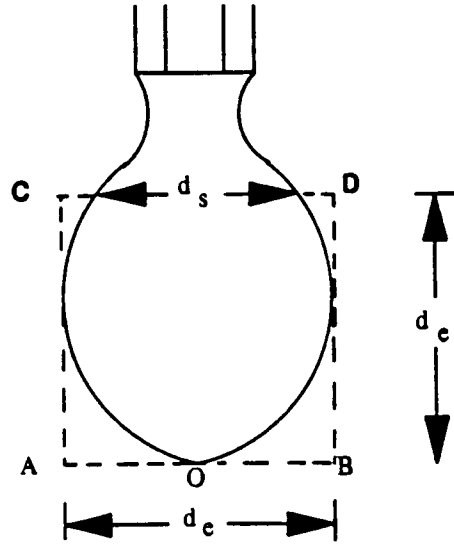
Figure 4.5: Profile of Pendant drop

$$p \propto \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \tag{4.15}$$

or

$$p = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \tag{4.16}$$

where γ is the interfacial tension in dynes/cm. This equation is known as the Laplace equation.

If y is the vertical height of the liquid measured from the apex of the drop profile where the two radii of curvatures are equal to each other i. e. $R_1 = R_2 = h$, then the hydrostatic pressure due to the curvature of the hanging drop at any point is given by:

$$p = \frac{2\gamma}{h} - \rho g y \tag{4.17}$$

Combining equations (4.16) and (4.17)

$$\gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2\gamma}{h} - \rho g y \tag{4.18}$$

where ρ is the density difference between the liquids in question. From geometry [40,42]–[45], the radii of curvature can be eliminated since,

$$R_1 = \frac{(1 + (\frac{dy}{dx})^2)^{3/2}}{\frac{d^2y}{dx^2}} \tag{4.19}$$

and

$$R_2 = \frac{x}{\sin\phi} = \frac{x(1 + (\frac{dy}{dx})^2)^{1/2})}{\frac{dy}{dx}} \tag{4.20}$$

Therefore

$$\frac{\frac{d^2y}{dx^2}}{\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{3/2}} + \frac{\frac{dy}{dx}}{x\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{1/2}} = \frac{2}{h} - \frac{\rho g y}{\gamma} \tag{4.21}$$

hence,

$$\frac{d^2y}{dx^2} + \frac{\frac{dy}{dx}}{x}\left[1 + \left(\frac{dy}{dx}\right)^2\right] = \left[\frac{2}{h} - \frac{\rho g y}{\gamma}\right]\left[1 + \left(\frac{dy}{dx}\right)^2\right]^{3/2} \tag{4.22}$$

This is a second-order, second-degree differential equation which cannot be integrated; however it can be simplified by transforming it into a non-dimensional form such as:

$$Y'' + \frac{Y'}{X}[1 + (Y')^2] = [2 - \beta Y][1 + Y'^2]^{3/2} \tag{4.23}$$

where

$$\beta = \frac{g\rho h^2}{\gamma} \tag{4.24}$$

and

$X = x/h$, $Y = y/h$, $Y' = dY/dX$, and $Y'' = d^2Y/dX^2$

From equation (4.24),

$$\gamma = \frac{g h^2 \rho}{\beta} \tag{4.25}$$

From literature [17,18,38,39,40], no method is known by which the dimensionless parameter β and the radius of curvature h can be precisely determined for a pendant drop from a picture of the drop.

In order to assign values to β and h so as to solve equation (4.24) for the interfacial tension, the following approach is adopted: consider a profile of the drop in figure 4.5 - the size of the drop is dependent on its equatorial diameter, d_e, and the shape is also dependent on the ratio of the diameters measured at two different horizontal planes. This approach was first suggested by Andreas et al. [38]. The maximum horizontal diameter d_e is the first measured, then by constructing the base line AOB, a parallel line CD, (d_s), is also drawn whose distance from AOB equals d_e. From the measured values of d_e and d_s, the shape ratio,

$$S = d_s/d_e \tag{4.26}$$

is computed for each drop profile. This value varies from drop to drop.

Another parameter, H, can also be defined as a function of the drop shape such that:

$$H = \beta \left(\frac{d_e^2}{h} \right) \tag{4.27}$$

$$= \rho g \frac{(d_e)^2}{\gamma} \tag{4.28}$$

H is considered to be a function of S. Tables of values of H as a function of S are available [39,40] from which γ can be quantified from the photograph. Rewriting equation (4.28)

$$\gamma = \frac{\rho g (d_e)^2}{H} \tag{4.29}$$

where ρ = density difference between the two liquids in question; g = acceleration due to gravity; d_e =equitorial diameter of the drop and is obtained from:

$$d_e = \left(\frac{w_o}{w_m} \right) d_e^m \tag{4.30}$$
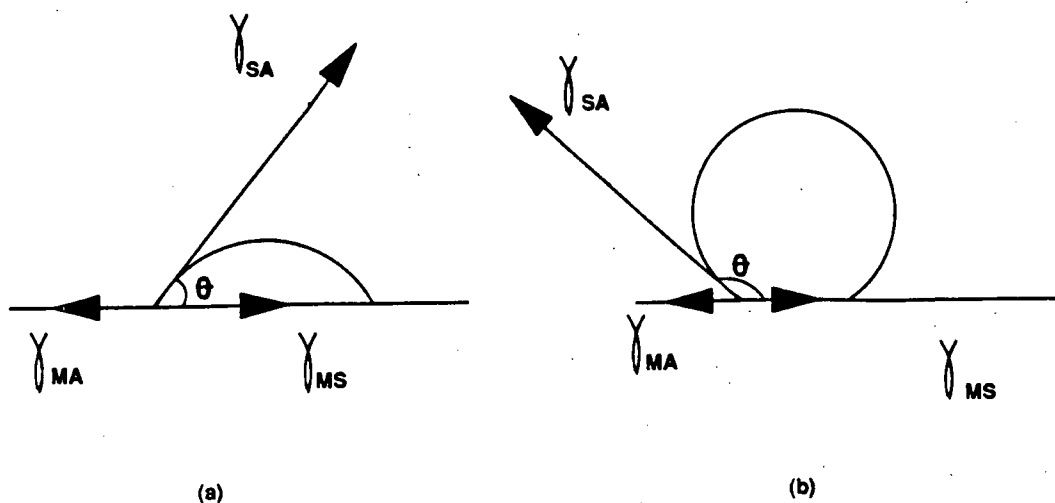
Figure 4.6: Contact Angle between a liquid and solid surface

where w_o = original diameter of the tip; w_m is the magnified diameter of the tip as measured from the photograph, d_e^m is the magnified diameter of drop as measured from the picture. Measurements and calculations require about 6–10 minutes per picture. The density of the liquid sulphur with temperature is obtained from literature: at 120°C it has a value of 1.8037g/cm^3, at 122°C it has a value of 1.8007g/cm^3, at 125°C its value is 1.7994g/cm^3 and at 130°C its value is about 1.7957g/cm^3. The density of the aqueous solutions are determined at room temperature and corrected for high temperatures (i. e. at the operating temperature) on the assumptions that the solutions have about the same coefficient of expansion as water (though this might introduce a slight error).

4.2 Contact Angles

These are measured directly from the photographs with a fair degree of accuracy. The contact angle that a liquid makes when it is at equilibrium with other phases in contact with it is related to the interfacial tensions or free energies per unit area of those phases,

such that, for sulphur in contact with marmatite mineral the two can be related as:

$$\gamma_{MA} = \gamma_{MS} + \gamma_{SA}\cos\theta \qquad (4.31)$$

and

$$\gamma_{MA} - \gamma_{MS} = \gamma_{SA}\cos\theta \qquad (4.32)$$

where γ_{MA} is the mineral - aqueous solution interfacial tension, γ_{MS} is the mineral - liquid sulphur interfacial tension, γ_{SA} is the liquid sulphur - aqueous solution interfacial tension, and θ is the contact angle measured in the liquid. The above equation is known as the Young's equation [11,14,38]–[41].

$\gamma_{MA} - \gamma_{MS}$ can be computed for the different systems. This will help us to determine if the surfactant is adsorbed at both mineral-sulphur and sulphur-aqueous solution interface. For no adsorption at the mineral surface, $\gamma_{MA} - \gamma_{MS}$ has to be constant for all systems irrespective of the aqueous enviroment.

4.2.1 Work of Adhesion

In the initial stages of zinc pressure leach, liquid sulphur is non-existent. However, it immediately begins to form in the system due to the reaction. In a continuous process, there is a steady state of liquid sulphur present at all times. The sulphur tends to displace the aqueous phase from the solid surface by adhesional wetting (i. e. liquid sulphur forms on the surface, or makes contact and adheres to the surface.) The surface free energy change associated with this wetting by liquid sulphur is:

$$-\Delta G_w = a(\gamma_{MA} + \gamma_{SA} - \gamma_{MS}) \qquad (4.33)$$

where a is the surface area of solid substrate (i. e. mineral) in contact with an equal surface of the liquid (sulphur) after adhesion. The driving force of this phenomena is $\gamma_{MA} + \gamma_{SA} - \gamma_{MS}$.

The work of adhesion, W_a, is the reversible work required to separate a unit area of liquid from the solid substrate.

$$W_a = \gamma_{MA} + \gamma_{SA} - \gamma_{MS} = -\Delta G_w/a \qquad (4.34)$$

This is known as Dupre's equation [13,21,40,41]. In this process, any reduction of the mineral - sulphur interfacial tension results in an increased tendency for adhesion to occur, but reduction of either the liquid-liquid or mineral-aqueous interfacial tensions decreases the adhesive tendencies.

From equation (4.32) above

$$\gamma_{SA}\cos\theta = \gamma_{MA} - \gamma_{MS} \qquad (4.35)$$

Substituting for $\gamma_{MA} - \gamma_{MS}$ in the W_a,

$$W_a = \gamma_{SA}\cos\theta + \gamma_{SA} \qquad (4.36)$$

$$= \gamma_{SA}(1 + \cos\theta) \qquad (4.37)$$

W_a can be computed from a knowledge of γ_{SA} and $\cos\theta$. The driving force in adhesional wetting can never be negative and is equal to zero only when the contact angle is $180°$, which is impractical.

Chapter 5

RESULTS AND DISCUSSION

5.1 RESULTS

5.1.1 Interfacial Tensions

All interfacial tension measurements recorded here are reproducible to ± 1 dyne/cm.
The interfacial tensions between aqueous solutions and liquid sulphur as a function of
pressure were measured for selected aqueous solution concentrations in the range 0.1 tō
1.8 molar. These measurements show that for any given concentration, the interfacial
tension remains almost unchanged over the entire pressure range (2 to 7 atmospheres)
studied. The measurements were made using solution concentrations between 0.1 and
1.8 molar. This agrees very well with observations made by earlier investigators that
pressure does not appreciably affect the liquid-liquid interfacial tensions (even over a
much larger pressure range).

At constant total pressure (6 atmospheres or 80 psi), the interfacial tensions varied
from 47 ± 1 dynes/cm for 0.1 molar $ZnSO_4$ solution to 54 ± 1 dynes/cm for 2.0 molar
solution. The results are shown in Figure 5.7 and listed in Appendix C Table C.13.

The interfacial tensions varied slowly from 47 ± 1 dynes/cm at 0.1 molar to 54 ± 1
dynes/cm at 1.5 molar, beyond which zinc sulphate concentration has no further notice-
able effect on the interfacial tensions.

With the introduction of the surface active agent (calcium ligninsulphonate), the
aqueous solution - liquid sulphur interfacial tensions drop from their maximum values

44

Effect of Solution concentration on
liquid-liquid Int. Tensions
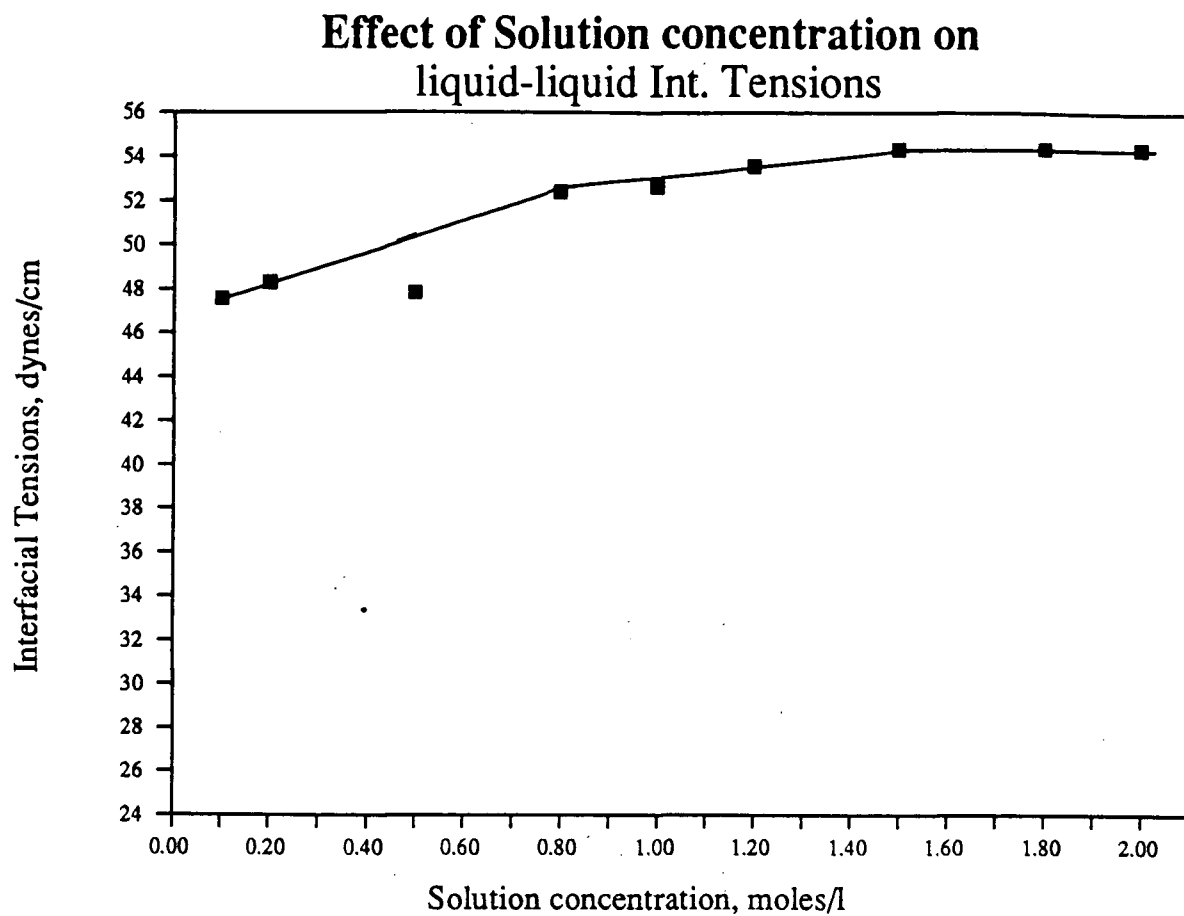
Figure 5.7: Liquid sulphur - Aqueous solution interfacial Tension versus Solution Concentration
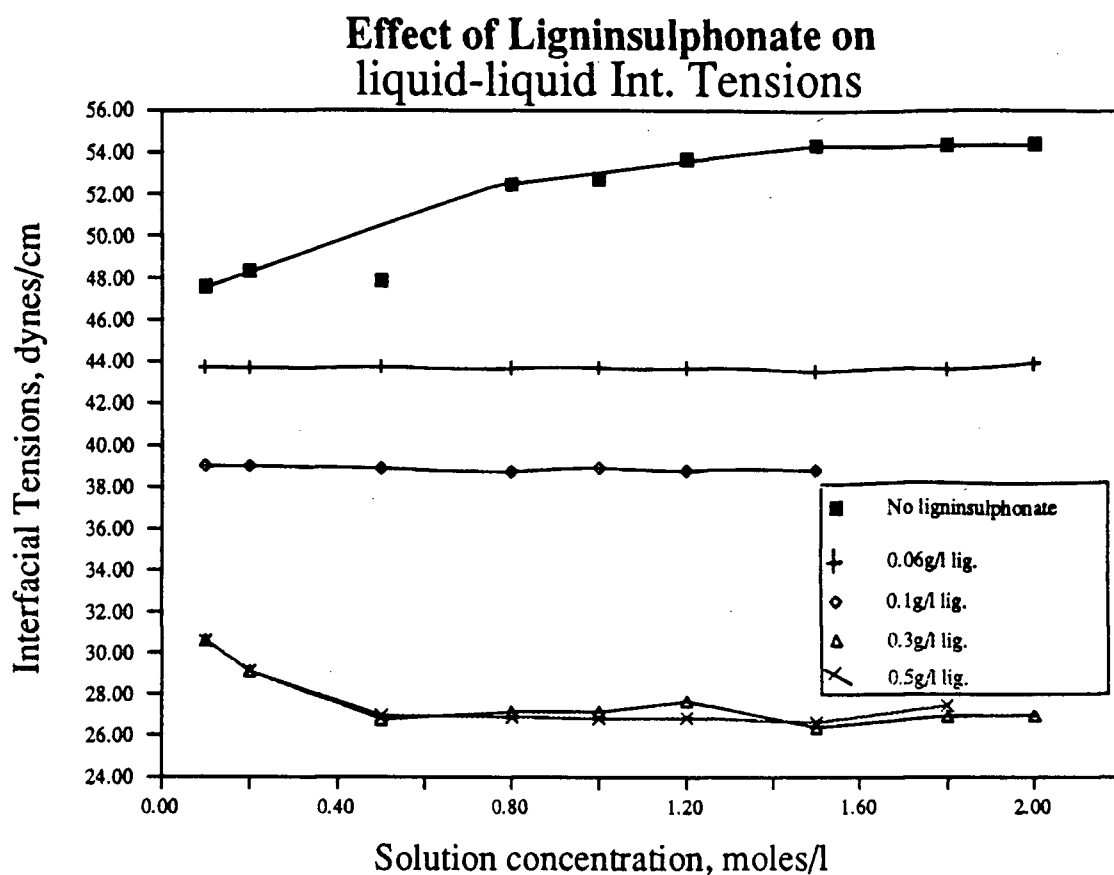
Figure 5.8: Effect of Surfactant concentration on the liquid sulphur - aqueous solution interfacial tensions.

attained (without surface active agent) to minimum values between 27-30 dynes/cm at 0.3 g/l ligninsulphonate concentrations. Any further increase in the surfactant concentration does not have any further effect on the liquid-liquid interfacial tensions. These are shown in Figure 5.8 and in Appendix C Table C.14

This means that 0.3 g/l ligninsulphonate is just enough to cause the maximum reduction in the liquid-liquid interfacial tensions. The presence of acid and iron (in the form of Fe^{2+} and Fe^{3+}) do not seem to have any noticeable effect (at least within the limits of the measurements employed) on the interfacial tension values, as seen in Tables 5.1 and

Table 5.1: Effect of Acid on Interfacial Tensions with and without Surfactant (0.3g/l)

Conc (molar)	Interfacial Tension, dynes/cm for:			
	sol'n only	sol'n + lig.	sol'n + acid (pH=0.4)	sol'n, acid and lig
0.1	47.6	30.6	53.6	28.1
1.5	54.3	26.4	53.7	27.3
1.8	54.4	26.9	53.3	24.4

Table 5.2: Effect of acid (pH=0.4) and Ferric/Ferrous ions on Interfacial tension

Solution Conc. (molar)	Interfacial Tension dynes/cm
0.1	53.6
1.0	54.2
1.5	54.3

5.2.

However, the effect of Fe^{3+}/Fe^{2+} on the efficiency of the surfactant is significant, especially with respect to time. Table 5.3 shows how the surfactant degrades with time in the presence of ferric/ferrous ions in one of the measurements made, where t is the time in minutes which elapsed after introducing the Fe^{3+}/Fe^{2+} into the system before the photographs were taken of the pendant drops.

Table 5.3: Effect of Fe^{3+}/Fe^{2+} on the Surfactant Efficiency in 1.5 molar zinc sulphate solution at pH=0.4

Time	$0 < t < 2$	$3 < t < 5$	$t > 5$
γ(dynes/cm)	27.2	30.5	36.9

Effect of source of surfactant on
liquid-liquid interfacial tensions
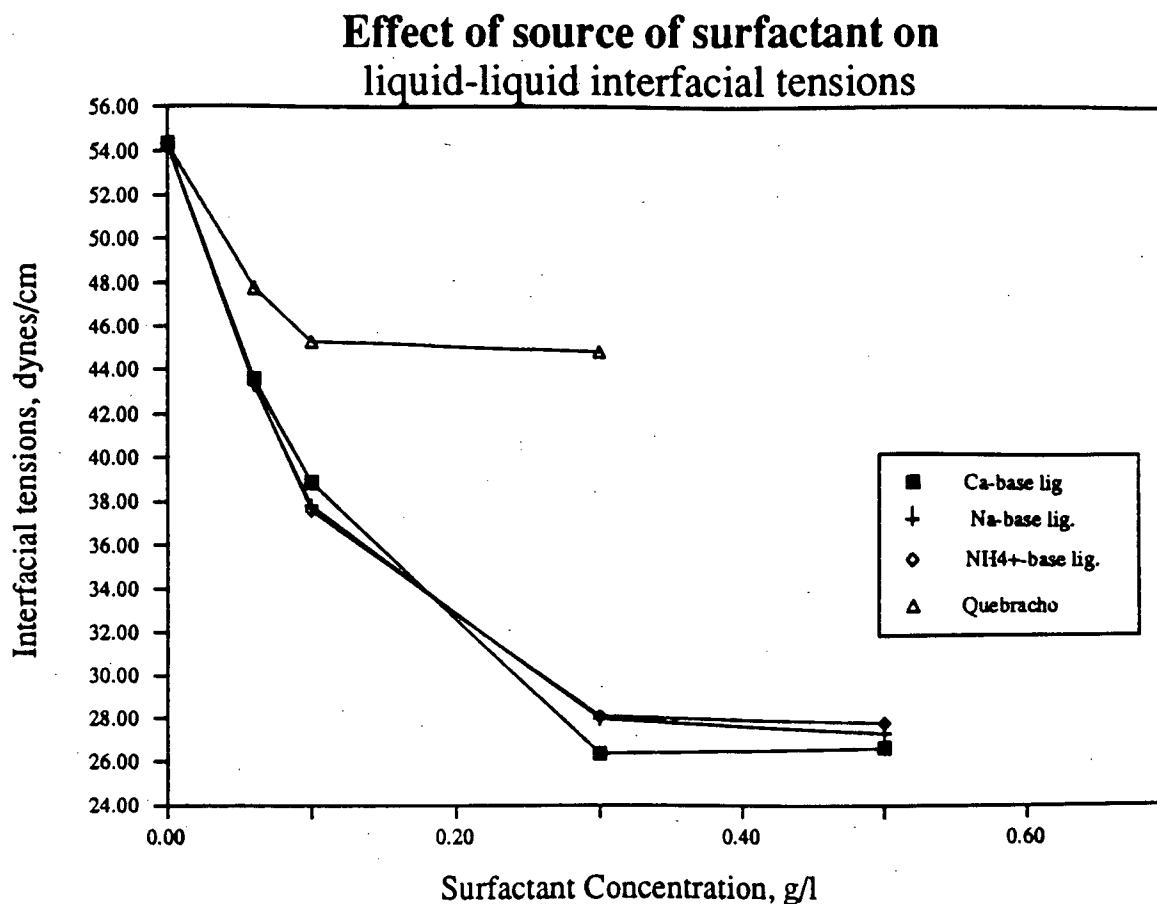
Figure 5.9: Effect of Surfactant Source on Liquid sulphur - Aqueous solution Interfacial Tensions in 1.5 molar zinc sulphate solution

Identification of Surfactants

Results obtained from measurements indicate that provided the effective ligninsulphonate concentration is the same, the source of the surfactant is not important. This is shown in Figure 5.9 and Table C.15 in appendix C where the effect of surfactants of three different origins were investigated.

Table 5.4: The effect of Quebracho in the presence of 0.3g/l ligninsulphonate in 1.5 molar Zinc sulphate solution

Ligninsulphonate Type	Concentration	
	0.1g/l Quebracho	0.3g/l Quebracho
Ca-base	28.1	27.7
Na-base(XD)	27.6	27.8
NH_4^+-base (TSD)	27.8	27.0
NH_4^+- base (NST - 150)	27.4	28.2

Effect of Quebracho

Quebracho is a form of ligninsulphonate that it is obtained directly from the bark of trees. By itself, quebracho lowers the surface tension to a much smaller extent than does ligninsulphonate (Figure 5.9 and appendix C Table C.16). Measurements were also made using ligninsulphonate to which quebracho was added as a supplementary surfactant. The result obtained (Table 5.4) shows that in the presence of the ligninsulphonate, the quebracho has no noticeable effect on the liquid-liquid interfacial tensions.

When quebracho was added to a solution, it was found to produce a visible suspension (at room temperature) in the solution. However, with increasing temperature of the system, the suspension seemed to dissolve and the solution turned yellowish in colour.

Effect of Tergitol

Tergitol is a non-ionic, greasy, organic solvent which is known to reduce the efficiency of pressure leaching when present in the system [46]. It is a derivative of ethylene oxide, a non-ionic surfactant and an ethoxylate of secondary alcohols. The effect of this chemical

Table 5.5: Effect of Tergitol on Interfacial tensions

Surfactant concentration	0.5g/l Tergitol	1.0g/l Tergitol	0.5g/l Tergitol + 0.5g/l Ca-lig	0.5g/l Tergitol + Fe 0.5g/l Ca-lig
γ dynes/cm	42.5	41.6	28.0	27.3

on the liquid-liquid interfacial tension and on the liquid sulphur-mineral contact angle was investigated. This surfactant is highly insoluble in the aqueous phase and floats on the surface of the aqueous solution when introduced. On gently stirring the solution, it was dispersed in the aqueous phase, and, vigorous shaking or stirring turned the whole solution cloudy. When present in high dosages, the aqueous solution turned cloudy the moment the tergitol was introduced. When ligninsulphonate was introduced, the tergitol immediately destroyed any foam due to the presence of ligninsulphonate. However, when added independently, both formed foam readily on shaking. The tergitol quickly spreads over the surface of any solid material that comes in contact with it. Table 5.5 shows the effect of tergitol on the interfacial tensions in 1.5 molar zinc sulphate acidified solution (pH=0.4).

Contact Angles

Contact angle measurements were made between liquid sulphur and a zinc sulphide mineral (marmatite) or pyrite under a variety of aqueous environments (in 1.5 molar zinc sulphate solution). Accompanying pictures in Figure 5.10 show the shape of a drop of sulphur resting on the surface of a marmatite mineral specimen in an aqueous environment with and without ligninsulphonate.

Tables 5.6 and 5.7 show some of the contact angle measurements made.
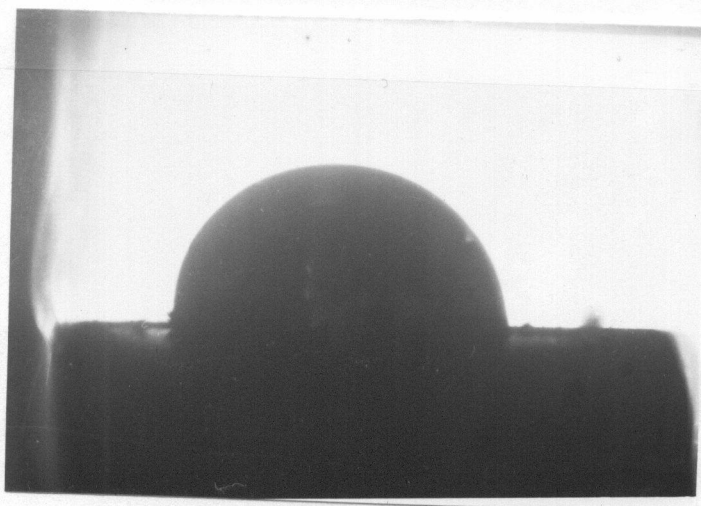
(a)

(b)

Figure 5.10: Shape of liquid Sulphur resting on marmatite mineral surface a) without any lignosol b) with 0.3g/l lignosol in solution.

Table 5.6: Liquid Sulphur - marmatite contact angles

Mineral	Marmatite				
Aqueous Environment	Sol'n only	sol'n + 0.3g/l lig	sol'n pH=0.4	sol'n pH=0.4 Fe	sol'n pH=0.4 Fe + 0.3g/l lig
θ	80 ± 5	143 ± 5	110 ± 6	101 ± 5	148 ± 6

Table 5.7: Liquid sulphur - pyrite contact angles

Mineral	Pyrite				
Aqueous Environment	sol'n only	sol'n + 0.3g/l lig.	sol'n pH=0.4	sol'n pH=0.4, Fe	sol'n pH=0.4 Fe + 0.3g/l lig
θ	76 ± 6	150 ± 4	113 ± 4	118 ± 5	150 ± 4

An attempt was made to investigate the extent to which quebracho also influences the liquid sulphur - marmatite mineral contact angle. Table 5.8 shows some of the measured values.

These contact angle values enable us to determine if the quebracho influences only one interface or both. The contact angles also give us an idea about how much energy is necessary to remove a drop of liquid sulphur of unit area from the surface of the mineral (which is applicable in industrial situations)

From the measurements made to determine the influence of tergitol on the mineral - liquid sulphur contact angles, it was observed that the presence of ligninsulphonate does not have any appreciable impact on the contact angles in the presence of the tergitol. Thus, the tergitol seems to suppress the ability of the ligninsulphonate to get adsorbed onto the mineral surface so as to increase the solid - liquid sulphur contact angles; hence

Table 5.8: Influence of quebracho on liquid sulphur-marmatite contact angles in 1.5 molar solution

Surfactant concentration	0.3g/l quebracho	0.3g/l quebracho + 0.3g/l lig	0.3g/l quebracho + 0.3g/l lig (pH=0.4, Fe^{3+}/Fe^{2+})
θ	126 ± 4	156 ± 6	158 ± 6

Table 5.9: Contact angle measurements in the presence of tergitol and lignosol in 1.5 molar solution at pH=0.4

Surfactant	0.5/l tergitol	0.5g/l tergitol 0.3g/l lig
θ	105 ± 5	107 ± 5

the presence of the tergitol increases the tendency of the sulphur to spread on the mineral surface and thus occlude the surface, making the mineral particle less accessible to leaching by the aqueous environment and as well increasing the retention time required for the process to go to completion. Table 5.9 and Figure 5.11 show the ineffectiveness of lignosol on a system containing tergitol.

5.2 DISCUSSION

All measurements were made manually. The results obtained from the measurements indicate the role the surfactants play in the zinc pressure leaching technology. The reduction of the liquid-liquid interfacial tension from maximum value of 54-55 dynes/cm to 27-30 dynes/cm at a ligninsulphonate concentration of 0.3g/l seems to be just enough for the process, though this may be considered to be small compared to the work of domestic
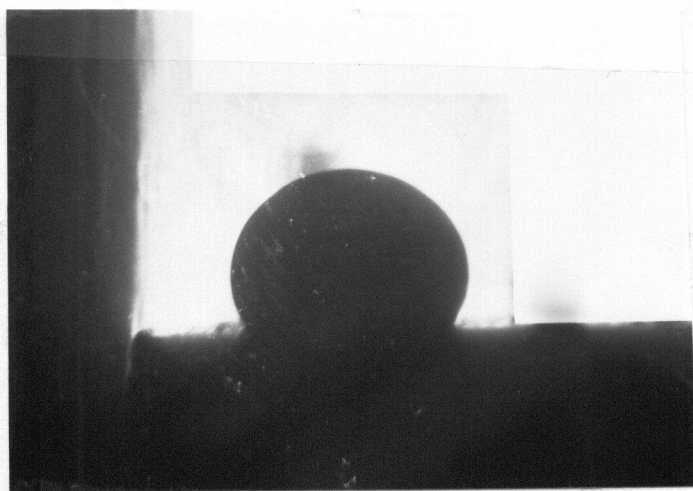
(a)
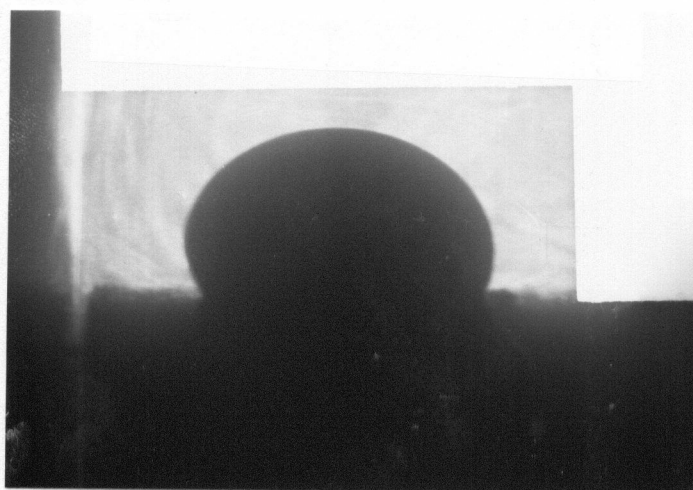
(b)

Figure 5.11: Photographs showing liquid sulphur resting on marmatite in 1.5 molar acidified solution in the presence of 0.5g/l tergitol a) without lignosol b) with 0.3g/l lignosol

detergent as applied for cleaning purposes. Combined with the ability to increase the liquid sulphur-mineral contact angle, the ligninsulphonate 'rolls' the liquid sulphur film into droplets which are easily removed from the solid surface and dispersed in the liquid as a result of the continuous agitation of the slurry. This is the basic principle underlying the removal of liquid sulphur from the solid surface and making the latter accessible to the aqueous leaching solution. The sulphur is then recoverable, either by coalescence under pressure above $120°C$, or by flotation. The use of a more efficient surfactant could be considered (if it is available) in which case the interfacial tensions would be lower and the contact angles increased for better sulphur detachment from the surface. However, there is a possibility that the sulphur might be so finely dispersed in the liquid that the subsequent recovery will be more difficult and expensive.

It can be inferred from the contact angles and the interfacial tension values that the ligninsulphonate when introduced into the system (in the zinc pressure leaching process) is adsorbed at both solid-liquid and liquid-liquid interfaces. From equation 4.32:

$$\gamma_{MA} - \gamma_{MS} = \gamma_{SA}\cos\theta$$

if the ligninsulphonate is adsorbed at only the liquid-liquid interface then γ_{MA} and γ_{MS} must be unchanged by the surfactant and $\gamma_{MA} - \gamma_{MS}$ must also remain unchanged, leading to a constant value for $\gamma_{SA}\cos\theta$ under all aqueous environmental conditions. The data obtained, table 5.10 indicate that $\gamma_{SA}\cos\theta$ is not constant, but varies with solution composition, confirming that the ligninsulphonate adsorbs at the liquid sulphur -aqueous solution as well as the liquid sulphur-mineral and aqueous solution-mineral interfaces. However, the absolute values of γ_{MA} and γ_{MS} cannot be computed from this data. Their computation will need an independent experimental technique which is outside the scope of this work.

The introduction of the surfactant into the system reduces the adhesional work, W_a,

Table 5.10: Values of $\gamma_{MA} - \gamma_{MS}$

Mineral	Marmatite				
Aqueous Environment	Sol'n only	sol'n + 0.3g/l lig	sol'n pH=0.4	sol'n pH=0.4 Fe	sol'n pH=0.4 Fe + 0.3g/l lig
$\gamma_{SA}\cos\theta$	9.4	−21.1	−18.4	−10.4	−23.1

Table 5.11: Adhesional work in the presence of 0.3g/l ligninsulphonate in 1.5 molar solution

Aqueous condition	sol'n only	sol'n + lig.	sol'n + Fe pH=0.4	sol'n + Fe + lig, pH=0.4
W_a	63.7	5.3	43.9	4.6

required to remove the liquid sulphur from the mineral surface. This implies that in the commercial process, less agitation energy is required than in a process without any surfactant. The work of adhesion, according to the equation 4.36

$$W_a = \gamma_{SA}(1 + \cos\theta)$$

decreases as γ_{SA} decreases and as θ increases from 0 to 180°. W_a can be computed for the different conditions. e. g. for $\theta = 80 \pm 5°$, and $\gamma_{SA} = 54.3$ dynes/cm (in a 1.5 molar solution) for the case where there is no ligninsulphonate in the system, and $\theta = 143 \pm 5°$, and $\gamma_{SA} = 26.4$ dynes/cm for the situation where 0.3g/l ligninsulphonate is present in the system, the two values of W_a are respectively 63.7 and 5.3 ergs/cm². The data shows that less energy is required to remove sulphur from the mineral surface in the presence of both ligninsulphonate and quebracho as is shown in tables 5.11 and 5.12.

At the operating temperatures of $125 \pm 4°C$ a neutral zinc sulphate solution undergoes

Table 5.12: Adhesional work in the presence of 0.3g/1 ligninsulphonate and 0.3g/1 quebracho in 1.5 molar solution.

| Aqueous condition	quebracho	Quebracho and lig	Quebracho + lig pH=0.4,Fe^{3+}/Fe^{2+}
W_a (joules)	18.6	2.4	2.1

the following reaction:

$$ZnSO_4 + H_2O \longrightarrow Zn(OH)_2 + H_2SO_4 \qquad (5.38)$$
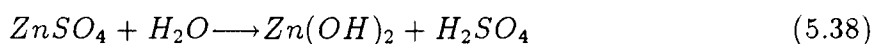
This might explain why the data collected show that the introduction of sulphuric acid seems not have any adverse effect on the interfacial tensions, especially at high concentrations of zinc. At the operating conditions, there is enough sulphuric acid present in the system to prevent hydrolysis of zinc. With the introduction of acid (pH=0.4) into the system, the liquid-liquid interfacial tensions for the lower concentration solutions (e. g. 0.1 molar) increased slightly from about 47 to 54 dynes/cm to equal the values obtained for the high concentration solutions (54 ± 1 dynes/cm) with and without acid. At room temperature the pH of the solutions were measured to be: 0.1 - pH=5.18. 0.2 - pH=5.25, 0.5 - pH=5.21, 0.8 - pH=5.16, 1.0 - pH=5.05, 1.2 - pH=5.02, 1.5 - pH=5, and 1.8 - pH=4.71. The presence of sulphuric acid introduced externally does not help either to increase or decrease the interfacial tensions to any extent. It's basic responsibility is to hold the Fe^{3+} ions in solution, since Fe^{3+} hydrolyses at high pH's and temperatures according to equation 1.7:

$$3Fe_2(SO_4)_3 + PbSO_4 + 12H_2O \longrightarrow PbFe_6(SO_4)_4(OH)_{12} + 6H_2SO_4$$
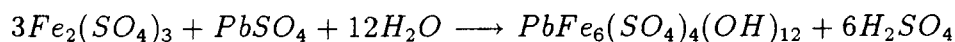
However, the acid seems to have some effect on the solid-liquid contact angle. There are two schools of thought which might explain this phenomena. The first of these is that

the $Zn(OH)_2$ produced according to reaction 5.40 may be deposited on the solid surface and this can have an adverse effect on the contact angles. The other explanation could be the direct effect of the acid on the mineral surface.

The introduction of Fe^{3+}/Fe^{2+} ions into the system did not have any influence on the interfacial tension values and did not introduce any appreciable changes (within a fair degree of accuracy) in the contact angles. Thus, it could be concluded that the function of the Fe^{3+}/Fe^{2+} as used in the zinc pressure leaching technology is to help transport the oxidizing power of dissolved oxygen to the mineral surface, and plays no other role.

Presence of Quebracho

The presence of quebracho in the system, theoretically, reduces the amount of energy required to remove a sulphur drop of unit surface area from a mineral surface of the same surface area. From the contact angle measurements made, this value is reduced to almost 50 % of that obtained without any quebracho in the system. However, from the liquid-liquid interfacial tension measurements made, (determined to within ± 1 dyne/cm), the quebracho does not affect any significant changes in the interfacial tension values in the presence of the ligninsulphonate. This must be attributed to adsorption of quebracho on the aqueous solution - mineral interface, supplementing or substituting for lignosol and lowering γ_{MA} thereby. Thus, any interfacial tension changes observed at the liquid-liquid interface is due to the work of the ligninsulphonate only. However, at the mineral surface, the quebracho competes successfully with the ligninsulphonate to the extent that both play some role in modifying the solid surface.

Source of Ligninsulphonate

Results obtained so far have shown that the origin of the ligninsulphonate is not important as long as the effective surfactant remains the same. This supports earlier observation

made by Xia Guang-Xiang et al. [3]. Measurements made using three different salts of ligninsulphonate may throw some light on the role of the cation i. e. Ca^{2+}, Na^+, NH_4^+, etc. It can be concluded from the available data that the cation does not play any active role in the process of interfacial tension reduction and hence in the mineral surface cleaning process in the zinc pressure leach. The whole process of interfacial/surface tension reduction and hence of the mineral surface renewal process may be due solely to the work of the ligninsulphonate anions. It is considered an anionic surfactant although its negative charge is probably protonated in acidic solutions, at these low pH values.

Presence of Tergitol

Tergitol, when present in zinc pressure leaching is known to reduce the efficiency of the process [46]. Investigations carried out in the laboratory so far indicate that the presence of tergitol in the slurry does not affect the efficiency of the ligninsulphonate at the liquid-liquid interface. However, it introduces a lot of changes at the liquid sulphur-marmatite mineral interface. Thus, it can be concluded that, at the liquid-liquid interface, the tergitol molecules are incapable of competing with ligninsulphonate for positions on the interface. However, at the liquid-mineral interface, it successfully interacts with the ligninsulphonate to the extent that it also renders the ligninsulphonate almost ineffective. In the presence of both ligninsulphonate and tergitol, the liquid sulphur-marmatite mineral contact angle increased from 80 ± 5 to about $107 \pm 5°$, essentially the same value ($105 \pm 5°$) which was obtained when only tergitol was used as the surfactant in the system. These figures give a picture of how tergitol can suppress the role of ligninsulphonate when both are present in the system (remembering that 148 ± 5 is the contact angle obtained for the case of lignosol only). The actual mechanism involved in tergitol behaviour is a matter of debate. It is known from Dreisinger et al. [4] that under pressure leaching

conditions, lignosol is degraded by ferric ions according to the reaction:

$$Fe^{3+} \; + \; lignosol \longrightarrow Fe^{2+} \; + degraded \; lignosol$$
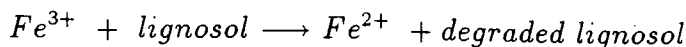
resulting in an increase in ferrous concentration at the end of the process. These experiments were repeated to determine the ferric/ferrous ratio in the presence of 0.3g/l lignosol (by itself) and 0.3g/l lignosol with 0.5g/l tergitol added as supplementary surfactant. The solution used for the experiment was 1.5 molar $ZnSO_4$ solution at a pH=0.4 containing 0.1 moles/l ferric ions and 0.022 moles/l ferrous ions. After 30 minutes of continuous agitation and heating (up to 135-140°C) in an autoclave and at about 6 atmospheres total pressure, the solution was immediately cooled in a bucket of cold water to 'arrest' the reaction, after which sample solutions were taken for volumetric analysis. The results were 0.028 moles/l Fe^{2+} for the case of lignosol only and 0.0274 moles/l for the condition where both tergitol and lignosol were present in the system. Within the measurement precision, these results are the same. The data indicate that the degradation of lignosol by ferric ions is not affected by the presence of tergitol, i. e. if a tergitol - lignosol compound exists, the lignosol end is just as reactive to ferric ions as in lignosol alone. It can be said with some degree of certainty that the tergitol spreads over the mineral surface, and the ligninsulphonate does not have enough detergent power to remove it. This assumption is consistent with earlier observations made by Schwuger and Smolka [48]: that a study of the adsorption of a mixture of anionic and nonionic (derivative of ethylene oxide) surfactants on charcoal showed that the adsorption isotherm of the nonionic was only slightly altered by the anionic, although the adsorption of the anionic surfactant was markedly affected by the former. Jayson et al. [49] and Rosen et al. [50] have also reported from their investigations on gas - aqueous solution systems containing mixtures of anionic and nonionic (derivatives of ethylene oxide) that at the gas - liquid interface the nonionic surfactant (normally with lower critical micelle concentration) exhibits greater surface

activity. These are supported by the mole fraction values computed for the interfacial surfactant concentrations which indicate low values for the anionic surfactant, especially at low anionic surfactant concentrations. Relating these earlier observations to the data and information obtained from the experiments carried out in the laboratory, one can say that at the marmatite - aqueous solution interface, the ligninsulphonate functional group is displaced by the nonionic tergitol molecules, although the mechanism by which this occurs is not clear.

Another possible effect due to the presence of the tergitol in the system might be due to changes in the surface characteristics of the solid mineral as the reaction proceeds with time. It is known that the surface properties of certain solids (or surfaces) involved in a given process keep changing as the process proceeds. Thus, a surface which forms a large contact angle with a liquid (or liquid sulphur) with which it is in contact (i. e. low adhesional energy) at the initial stages of the process can undergo some changes during the course of the reaction such that (probably) halfway through the process, changes in surface properties result in corresponding changes in the contact angles (either an increasing or decreasing in the contact angles). In the zinc pressure leach, if these changes correspond to decrease in the contact angles the sulphur spreads over the mineral surfaces and this increases the retention time of the process. Hence, the observations which have been made in the zinc pressure leaching (in the presence of tergitol) may be explained by one or combination of these two phenomena i. e. :

- that tergitol spreads over the mineral surface and displaces lignosol.

- that in the presence of the tergitol the surface properties of the mineral undergo changes with time (such as would occur if the reactivity of different crystal planes in marmatite were altered).

Thus, in the presence of tergitol, more adhesional work has to be done to remove a

sulphur droplet of unit surface area from the surface of a mineral of the same area when compared to the situation when only ligninsulphonate is present as surfactant.

Chapter 6

CONCLUSIONS AND RECOMMENDATION

6.1 CONCLUSIONS

The measurements made in this text have identified the role of the surfactant in the zinc pressure leaching process. The conclusions are all drawn from experimental observations made or measured and, where necessary, compared with results made by other investigations or found in industrial practice. Based on the measurements made, the following conclusions are made:

a) 0.3g/l lignosol is enough to cause a maximum reduction in the liquid sulphur - aqueous solution interfacial tensions and it is not certain that the maximum reduction is achieved at exactly 0.3g/l. It lies anywhere between 0.1 and 0.3g/l. This agrees well with commercial practice where a surfactant concentration of between 0.1 and 0.3g/l is added continuously to the mineral slurry. Thus, it can be concluded from this investigations that the surface coverage of marmatite and liquid sulphur by ligninsulphonate is essentially complete at 0.3g/l surfactant.
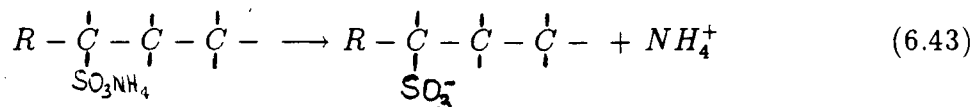
b) with the introduction of the quebracho as a supplement to lignosol, the liquid sulphur-aqueous solution interfacial tension remains unchanged, and the explanation for this behaviour is that the lignosol successfully competes with the quebracho to occupy positions on liquid sulphur. However, at the mineral-aqueous interface, it plays an effective role in the interfacial phenomena. The reason for this behaviour might be due to the orientation of the molecules at the solid surface, or to several types of surface sites

on the solid. It is probable that at the mineral-aqueous solution interface, the molecules orient themselves such that their hydrophilic ends are directed into the aqueous phase and thereby reducing the mineral - aqueous solution interfacial tension and increasing the mineral-liquid sulphur interfacial tensions (thereby speeding up the detachment process). The effective roles played by both lignosol and quebracho at the mineral-liquid interface are then additive. The same cannot be said of the quebracho at the liquid-liquid interface where the data collected indicate that the lignosol displaces the former from the interface or render it ineffective even if it is able to occupy sites at the interface. The explanation for this behaviour of quebracho might be that : under the influence of the lignosol electric charge (or ionic structure), the quebracho molecules migrate into the liquid sulphur instead of stationing themselves at the interface whereas at the mineral-liquid interface this migration of the quebracho molecules into the mineral is not feasible since the mineral is not penetrable. Hence the quebracho molecules tend to stay on the solid surface thus affecting to some degree the mineral-liquid interfacial properties. A quebracho concentration of 0.1g/l (by itself or as a supplement) was enough to induce the maximum interfacial tension reduction. Any dosage greater than this did not introduce any further change.

c) the role of sulphuric acid in the system is to keep Fe^{3+} ions in solution. The data collected show that the introduction of acid into the system did not change the liquid-liquid interfacial tensions both with and without ligninsulphonate. An earlier observation made by Dreisinger et al. in zinc pressure leaching indicated that an increase in the acid concentration did not affect the rate of zinc extraction. However, it did increased the contact angles to some degree. The small effect on the contact angle by acid is most likely due to the elimination of hydrolysis product such as $Zn(OH)_2$ and hydrolysed ferric species from the mineral surface.

d) Ligninsulphonates belong to the sulphonic acids group and hence possess some of

the characteristics of these acids. They ionize according to:

$$R - \overset{|}{\underset{\underset{SO_3H}{|}}{C}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \ + H_2O \ \longrightarrow \ R - \overset{|}{\underset{\underset{SO_3^-}{|}}{C}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \ + H_3O^+ \tag{6.41}$$

$$R - \overset{|}{\underset{\underset{SO_3Na}{|}}{C}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \ \longrightarrow \ R - \overset{|}{\underset{\underset{SO_3^-}{|}}{C}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \ + Na^+ \tag{6.42}$$

$$R - \overset{|}{\underset{\underset{SO_3NH_4}{|}}{C}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \ \longrightarrow \ R - \overset{|}{\underset{\underset{SO_3^-}{|}}{C}} - \overset{|}{\underset{|}{C}} - \overset{|}{\underset{|}{C}} - \ + NH_4^+ \tag{6.43}$$
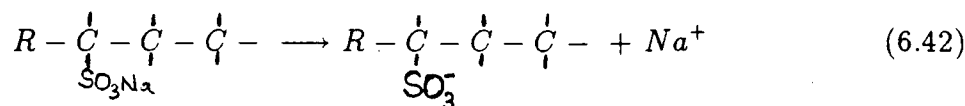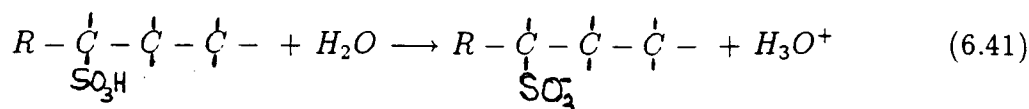
For anionic surfactants, the active component for cleaning purposes is the negatively charged ion, hence for the ligninsulphonate acids/salts, the active component for cleaning purposes is the negatively charged ligninsulphonate ion. Thus, the cation (i. e. Na^+, Ca^{2+}, NH_4^+, H^+, etc.), plays no major role in the cleaning processes performed by the ligninsulphonate acids/salts. The data indicate that, provided the effective lignosol remains the same, the identification of the salt/acid is not important.

e) from the values computed for $\gamma_{SA}\cos\theta$ (or $\gamma_{MA} - \gamma_{MS}$), it is clear that lignosol is adsorbed at both liquid sulphur-aqueous solution and mineral-aqueous solution interfaces. $\gamma_{SA}\cos\theta$ should be constant for the situation where there is no adsorption at the mineral - liquid interface in which case γ_{MA} and γ_{MS} will not be affected by the presence of the surfactant. However, this is not the case; $\gamma_{MA} - \gamma_{MS}$ varies with lignosol additions to the solution.

From $\gamma_{MA} - \gamma_{MS} = \gamma_{SA}\cos\theta$, the relative effect of lignosol can be visualized, though the absolute values can not be obtained. Referring to Table 5.10, in the presence of lignosol γ_{MS} far exceeds the value of γ_{MA} when compared to that obtained without lignosol, since a surfactant can only lower a surface tension, and not raise it. Therefore, γ_{MS} cannot be higher in the presence of lignosol, and the whole effect of the surfactant is on

γ_{MA} which is lowered. The combined effect of lignosol in lowering both γ_{MA} and γ_{SA} is to raise the contact angle and produce more spherically shaped sulphur drops on the mineral surface.[1] By assuming this shape, the tendency for the sulphur to detach (or roll) from the surface of the mineral is high, thus making the particle accessible to the aqueous solution. The presence of quebracho in the system helps to boost this property of the lignosol at the mineral-liquid interface. The quebracho reduces the adhesional work to about 50 % of the value obtained with lignosol only.

f) the mechanism by which tergitol suppresses the role of ligninsulphonate in the performance of its duties as a cleaning agent at the marmatite - liquid interface in the zinc pressure leaching is still uncertain. Most likely, tergitol adsorbs on the mineral more strongly than lignosol, displacing it, and having very small or no hydrophilic groups, it renders the mineral surface hydrophobic and sulphophilic (sulphur-loving). Tests conducted in the autoclave indicate that whereas the ligninsulphonate is degraded (oxidised) by ferric ions, the tergitol is neither degraded by ferric ions nor is there evidence that it reacts chemically with the ligninsulphonate. This rules out the question of the ligninsulphonate being destroyed by the tergitol in order to take over its functions. It can thus be supposed from these observations and that of earlier investigators [48,49,50] that the tergitol has the tendency to displace the lignosol from the mineral - liquid interface.

6.2 RECOMMENDATION

1. The pressure leaching of copper and other sulphide minerals can be given a serious new consideration, due to the environmental pollution problems associated with smelting and the roast-leach technologies currently being used, leading to emission
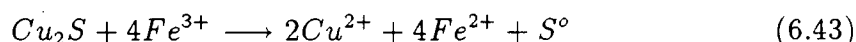
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[1]The spherical shape is actually enhanced by high liquid - liquid surface tensions. However, if the surface tension is lowered, it takes less work to make smaller drops, which are more spherical because of lower gravitational effects.

of sulphur dioxide gases. From laboratory studies [51] on the acid pressure leaching of copper sulphide minerals, in ferric ions solutions, the sulphur inhibition which characterised the zinc pressure leach in the absence of surfactant is evident when the process is carried out at temperatures above the melting point of sulphur. for covellite leaching the reaction is:
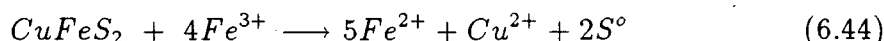
$$CuS + 2Fe^{3+} \longrightarrow Cu^{2+} + 2Fe^{2+} + S^{\circ} \tag{6.42}$$
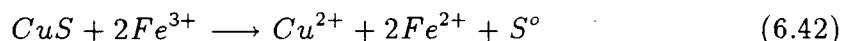
for chalcocite leaching the total reaction is:

$$Cu_2S + 4Fe^{3+} \longrightarrow 2Cu^{2+} + 4Fe^{2+} + S^{\circ} \tag{6.43}$$

and for chalcopyrite leaching, it is:

$$CuFeS_2 + 4Fe^{3+} \longrightarrow 5Fe^{2+} + Cu^{2+} + 2S^{\circ} \tag{6.44}$$

Thus, a suitable surfactant which will be applicable under the acid pressure leaching conditions should be developed if these processes are to achieve any meaningful success on commercial scale. At temperatures below the melting point of sulphur the retention time is too long and this can be reduced by raising the reaction temperature of the system (rate of reaction increases with increasing temperature).

Lignosol cannot be used as a surfactant in the pressure leaching of copper sulphide minerals because of the catalytic nature of cupric ions. In the absence of ferric ions, cupric ions (Cu^{2+}) can act as the oxidising agents in the zinc pressure leaching according to:

$$ZnS + 2Cu^{2+} \longrightarrow 2Cu^{+} + Zn^{2+} + S^{\circ} \tag{6.45}$$
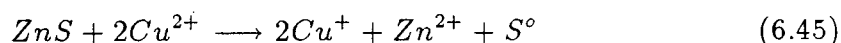
where the Cu^{+} ions regenerates Cu^{2+}. In copper leaching both Fe^{3+} and Cu^{2+} effectively combine and oxidise (degrade) the ligninsulphonate if it is used as a surfactant, thus destroying its usefulness. A surfactant much more resistant to oxidation, but with essentially the same surface active properties is needed.

2. An image analyser should be used to digitize the photographs if any further work is to be done on surface tension and contact angle measurements. This should increase the degree of precision of the measurements.

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Appendix A

Calibration of Equipment

Calibration of equipment for interfacial tensions was done using benzene and water at room temperature. The standard interfacial tension value for benzene and water at room temperature as given in literature [40] is 35 dynes/cm. Four calibration tests were performed and the values obtained were 34.98, 33.20, 34.00 and 34.42 dynes/cm; these give an average value of 34.15 dynes/cm.

Appendix B

Radii of Curvature

The derivation of these quantities are based purely on analytical geometry and applied to the pendant drop. The curvature, κ, of a curve at a point P(x,y) is the rate of change of ϕ per unit change in arc length along the curve at that point i. e.

$$\kappa \; = \; \left| \frac{d\phi}{ds} \right| , \qquad (B.48)$$

where ϕ is the angle in figure B.12 and s is the arc length measured along the curve. Radius of curvature is the reciprocal of curvature:

$$\sigma \; = \; 1/\kappa \qquad (B.49)$$

Thus, if one of these quantities is known, the other can be easily obtained. Consider the equation

$$p \; = \; \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \qquad (B.50)$$

where R_1 and R_2 are the radii of curvature. Consider the curve C (i. e. the profile of the pendant drop) to be represented by a twice differentiable function y = f(x). Let P(x,y) be any arbitrarily point on the curve, C, and ϕ is the inclination of the tangent to the curve at P (i. e. the angle between a tangent and the horizontal). At P, R_1 can be represented as being in the plane of the paper and R_2 perpendicular to the plane of the paper. R_2 is given by NP (on the diagram) which rotates about OO. At the apex (origin, O) $R_1 = R_2$. In two dimensional space, x, y, the direction
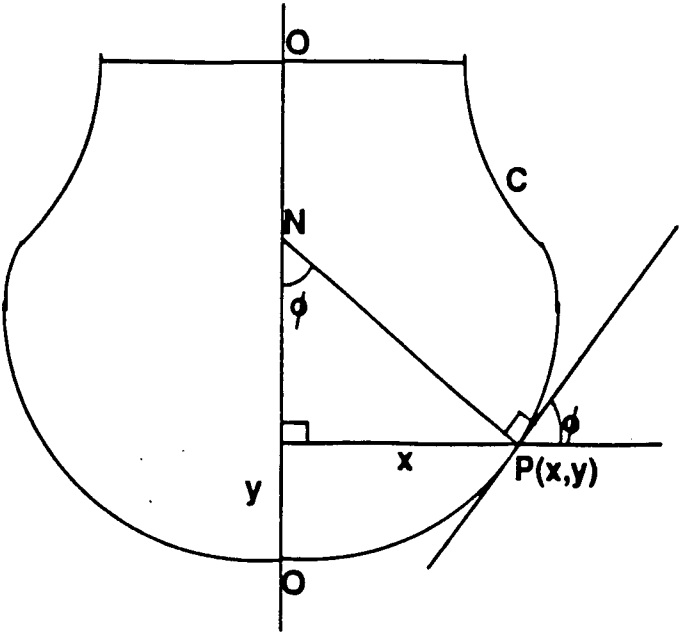
75

Figure B.12: Section of pendant drop profile

of a line is given by its inclination. The tangent to the curve at any arbitrarily point P is given by:

$$\tan \phi = f'(x) = y' \tag{B.49}$$

$$\Rightarrow \phi = \tan^{-1} f'(x) \tag{B.50}$$

Therefore, since

$$\kappa = \left| \frac{d\phi}{ds} \right| = \left| \frac{d\phi}{dx} \cdot \frac{dx}{ds} \right| \tag{B.51}$$

$$= \left| \frac{d}{dx} \tan^{-1} f'(x) \right| \left| \frac{dx}{ds} \right| \tag{B.52}$$

However (from calculus),

$$\frac{d}{dx} \tan^{-1} f'(x) = \frac{y''(x)}{1 + (y'(x))^2} \tag{B.53}$$

Meanwhile, $\frac{dx}{ds}$ can be derived from the curve considering the movement of P(x,y) such that

$$\frac{ds}{dx} = \sqrt{1 + (y'(x))^2} \tag{B.54}$$

$$\Rightarrow \kappa = \frac{y''(x)}{1 + (y'(x))^2} \frac{1}{\sqrt{1 + (y'(x))^2}} \tag{B.55}$$

$$= \frac{y''(x)}{\sqrt[3/2]{1 + (y'(x))^2}} \tag{B.56}$$

The radius of curvature R_1, can be obtained as the reciprocal of κ.

From figure B.12

$$R_2 = \frac{x}{\sin \phi} = \frac{x[1 + (y'(x))^2]^1/2}{y'(x)} \tag{B.57}$$

Appendix C

TABLES

Table C.13: Interfacial Tension between Aqueous Zinc Sulphate Solutions and Liquid Sulphur at 6 atmospheres total pressure and $125\pm4°C$

Zn conc(M/l)	0.1	0.2	0.5	0.8	1.0	1.2	1.5	1.8	2.0
γ(dynes/cm)	47.6	48.3	47.8	52.4	52.7	53.6	54.3	54.4	54.4

Table C.14: Effect of Surfactant concentration on Interfacial Tension

Surfactant conc(g/l)	Solution Concentration (moles)								
	0.1	0.2	0.5	0.8	1.0	1.2	1.5	1.8	2.0
0.06	43.7	43.7	43.7	43.7	43.7	43.7	43.6	43.7	43.9
0.1	39.0	39.0	38.9	38.8	38.9	38.8	38.9	-	-
0.3	30.6	29.0	26.8	27.2	27.2	27.7	26.4	27.0	27.0
0.5	30.6	29.1	27.0	27.0	26.8	26.9	26.6	27.5	-

Table C.15: The Effect of Ligninsulphonate Source on Interfacial Tensions in 1.5 molar zinc sulphate solution

Surfactant	Concentration, g/l				
Type	0.0	0.06	0.1	0.3	0.5
Ca-base ligninsulphonate	54.3	43.6	38.9	26.4	26.6
Na-base(XD) ligninsulphonate	54.3	43.3	37.8	28.0	27.3
NH_4^+-base(TSD) ligninsulphonate	54.3	43.4	37.6	28.1	27.8

Table C.16: Effect of Quebracho in 1.5 molar solution

Conc (g/l)	0.00	0.06	0.1	0.3
γ	54.3	47.8	45.3	44.8

Appendix D

FIGURES
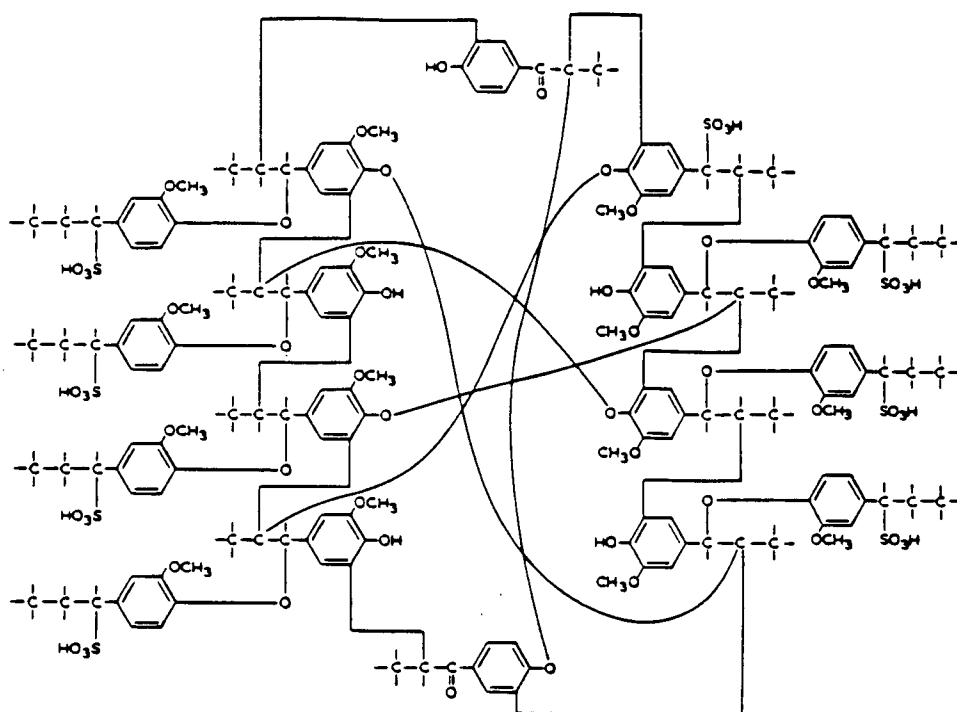
Figure D.13: Condensation Polymeric Structure of Ligninsulphonate
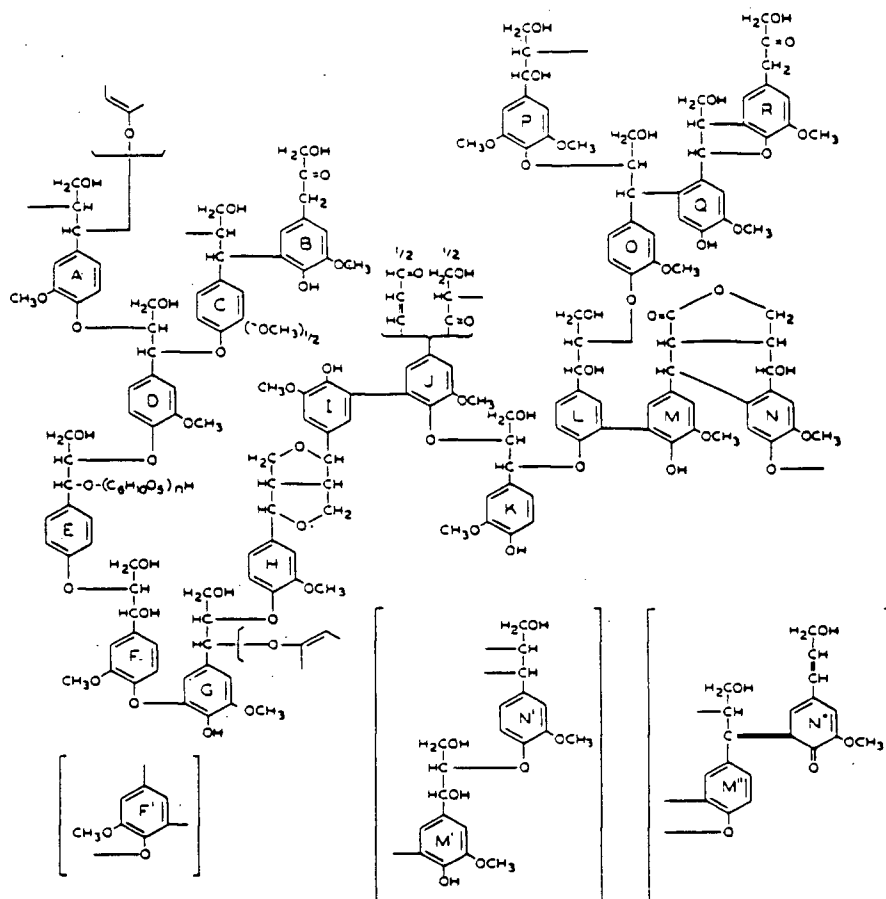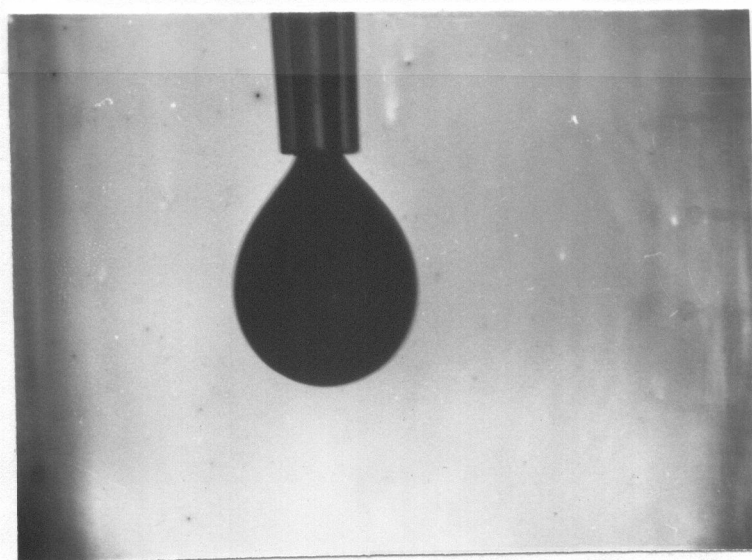
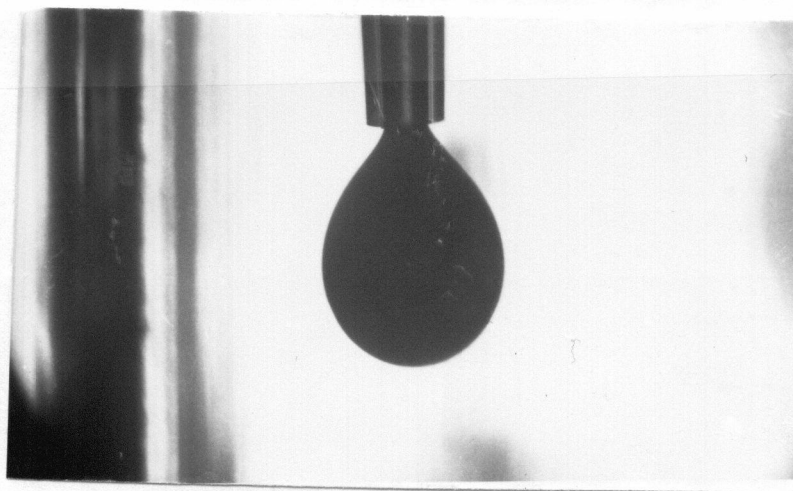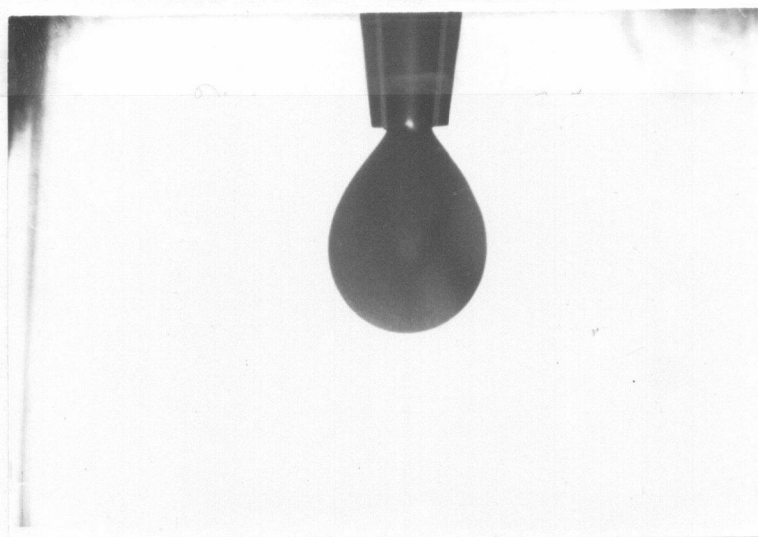Figure D.14: Freudenberg's 1965 formulation for lignin
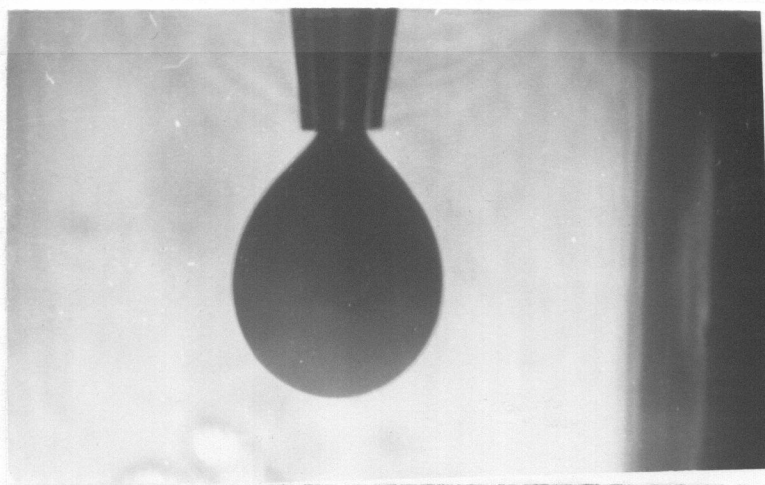
(a)

(b)

Figure D.15: Photographs showing pendant drops of liquid sulphur in 1.5 molar aqueous solution a) without lignosol b) with 0.06g/l lignosol (Ca-based)

(a)

(b)

Figure D.16: Photographs showing pendant drops of liquid sulphur in 1.5 molar aqueous solution a) with 0.1g/l lignosol b) with 0.3g/l lignosol (Ca-based)
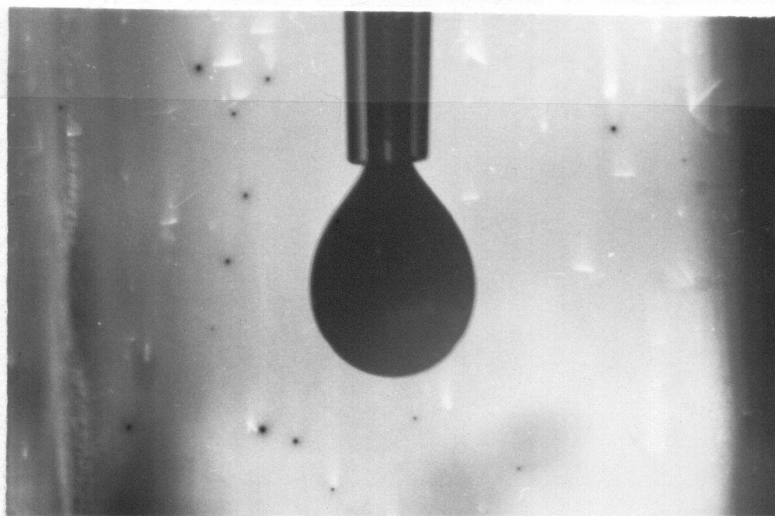
Figure D.17: Photograph showing a pendant drop of liquid sulphur in 1.5 molar aqueous solution with 0.5g/l lignosol (Ca-based)