



Effects of Additives in Froth Flotation of Silicate Zinc Ore; A Study by Zeta Potential Measurement and Infrared Spectroscopy

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ABSTRACT

Effects of sodium hexametaphosphate (NaPO_3)₆, sodium sulphide (Na_2S) and stearyl amine ($\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$) on froth flotation of a hemimorphite zinc ore were studied by zeta potential measurement and infrared spectroscopy. The results from zeta potential measurement confirmed the roles of (NaPO_3)₆ as anionic dispersant, Na_2S as anionic sulphidiser and pH regulator, and $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$ as cationic collector. Indirect effects of the adsorbed anionic species from the sodium hexametaphosphate and the sodium sulphide on the symmetry of Si-O and Zn-O bonds on the ore surface were successfully detected by infrared spectroscopy. These effects resulted in a shift of $\nu_s(\text{Si-O})$ and/or $\nu_a(\text{Si-O})$, and a shift or splitting of Zn-O stretching.

Keywords : flotation, zinc ore, additives, zeta potential, infrared spectroscopy.

1. INTRODUCTION

Froth flotation is an ore dressing method. Normally, the surface of ore particles in suspension are modified to be hydrophobic by adsorption of some additives. The air is flowed into the suspension forming bubbles on which ore particles are attached. These bubbles flood up to the surface of the suspension forming a film called “froth”, which can be collected as a concentrate. The bottom product is usually a tailing.

Among the additives, sodium hexametaphosphate (NaPO_3)₆ (Figure 1(a)) is a deflocculant widely used in clay industry [1]. It was also reported [2] to be the most effective reagent regarding an increase in the dispersion degree in calamine zinc ores

flotation. Sodium sulphide (Na_2S), which acts as a sulphidiser, can react with water; $\text{Na}_2\text{S} + \text{H}_2\text{O} = 2\text{Na}^+ + \text{H}_2\text{S} + 2\text{OH}^-$, and H_2S can dissociated according to the following reactions; $\text{H}_2\text{S} = \text{H}^+ + \text{HS}^-$ and $\text{HS}^- = \text{H}^+ + \text{S}^{2-}$ [3]. Totally, the amount of produced H^+ is still less than that of OH^- , the alkalinity of the solution is hence increased and the sodium sulphide also acts as a pH regulator. Salum et al. [4] studied the effects of sodium sulphide in flotation of silicate zinc ores, hemimorphite and willemite, and reported that the percentage of zinc recovery were increased by sodium sulphide addition. Stearyl amine ($\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$) (Figure 1(b)) was used as a cationic collector in zinc ore flotation [e.g. 4].

Since amine solubility in water is very low, therefore, it has to be neutralised by acetic acid in order to increase its solubility. Neutralisation consists in the formation of a primary amine salt, in which acetate from acetic acid is the anionic radical and the alkyl ammonium ion is the cationic counterpart; $(R-NH_3^+)(H_3C-COO^-)$ [5]. The acetate ion stayed away from

the inner interface region of the electrical double layer and/or in the bulk solution, thus behaving as an indifferent species [5]. In the case of flotation of hemimorphite and willemnite, it has been reported [4] that the percentage of zinc recovery by using stearyl amine as a collector was maximized at $pH = 10$.

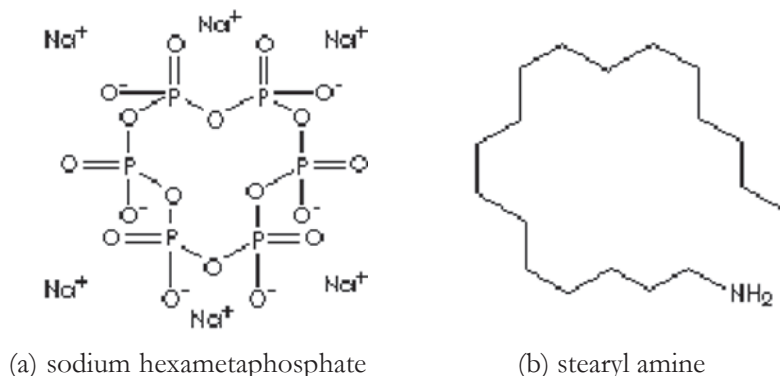


Figure 1. Structures of (a) sodium hexametaphosphate and (b) stearyl amine [6].

In Thailand, silicate zinc ore of hemimorphite type at Tak province is a raw material in production of zinc metal by hydrometallurgy and electrometallurgy. Sodium hexametaphosphate, sodium sulphide and stearyl amine have been used as additives in froth flotation. However, a study by zeta potential measurement and infrared spectroscopy on the effects of these additives in froth flotation of this ore has not been attempted and it is the objective of this work. The results can reflect some insight in the mechanism of these additives in froth flotation of silicate zinc ore.

2. EXPERIMENT

Silicate zinc ore obtained from Mae Sod district, Tak province, was ground and size screened to have particle size as required in each experiment. Sodium hexametaphosphate ($NaPO_3)_6$, hydrated sodium sulphide ($Na_2S \cdot 9H_2O$) and stearyl amine ($CH_3(CH_2)_{17}NH_2$) were used as additives.

Details of these chemicals are given in Table 1.

2.1 Zeta Potential Measurement

The ore, with particle size less than $2\mu m$, was weighted out as 0.1000 g and dispersed in 100 ml of the 0.001 M KCl solution. The suspension was sonicated at 40 kHz for 10 minutes. The pH of this suspension was measured. The Zeta-Meter 3.0 was used to measure the zeta potential of the ore particles in the suspension at various pH conditions. To study the effect of pH, the pH of the suspension was adjusted using 1 M HCl and 1 M NaOH solutions. To study the effect of $(NaPO_3)_6$, the $(NaPO_3)_6$ was added into the suspension in the range of 0.0002-0.5000 g/l. To study the effects of Na_2S and $CH_3(CH_2)_{17}NH_2$, the $Na_2S \cdot 9H_2O$ in the range of 0.0030-1.8750 g/l, was added into the suspension containing $(NaPO_3)_6$ 0.0010 g/l without and with addition of $CH_3(CH_2)_{17}NH_2$ 0.0005 g/l. The amount of $Na_2S \cdot 9H_2O$ was

varied up to 2 g/l. The amount of $(\text{NaPO}_3)_6$ and stearyl amine was fixed at 0.0010 g/l and 0.0005 g/l, respectively.

2.2 Infrared Spectroscopy

The ore, with particle size less than 200 μm , was weighted out as 500 g and suspended in 2 l of distilled water in a mechanical-type Denver flotation cell. The pulp was stirred at 1,300 rpm for 15 minutes before adding $(\text{NaPO}_3)_6$, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$ consecutively. Three flotation experiments were conducted. The contents of these additives in each flotation experiment were given in Table 2. Finally, pine oil ($\text{C}_{10}\text{H}_{17}\text{OH}$) of 0.02 ml/l (0.08 l/ton ore) was added as frother.

The concentrates in each flotation experiments, expected to carry on their surfaces the adsorbed species, were collected and dried in an electrical oven at 105°C over

night. They were consequently weighted out as 0.0030 g and mixed homogeneously with 0.0970 g of KBr in Agate mortar. The mixture was then pelletised at a pressure of 8-10 mPa for 3-4 minutes. Infrared spectroscopy was performed using a Perkin-Elmer Spectrum GX Spectrophotometer in the range of 4,000-400 cm^{-1} .

3. RESULTS AND DISCUSSION

3.1 Zeta Potential Measurement

Figure 2 shows the values of zeta potential of the ore particles in the suspension at various pH. The natural pH when the ore particles were suspended in the 0.001 M KCl was neutral i.e. 7.0 as marked by the circle in the figure. The zeta potential at this condition was about -26 mV. The zeta potential became more positive as the pH of the suspension was reduced. The point of zero charge was found at pH about 3.0.

Table 1. Detail of additives used in the experiment.

Additives	Suppliers	Essay
$(\text{NaPO}_3)_6$	Witcorp Chemicals Ltd.	total phosphate 68% min.insoluble matter 0.1% max.Fe 1 ppm max.
$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	Asian Scientific Co., Ltd.	sodium sulphide flake 60% min. Fe 0.12% max. Na_2CO_3 3.5% max. water insoluble matter 0.2% max.
$\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$	Clariant Chemicals (Thailand) Ltd.	amine value 205-216 mgKOH/g primary amine (equiv.) 96% min.

Table 2. The contents of additives in flotation experiments.

Additives	Flotation Experiments		
	I	II	III
$(\text{NaPO}_3)_6$	0.05-0.50 g/l (0.2-2.0 kg/ton ore)	0.25 g/l (1.0 kg/ton ore)	0.25 g/l (1.0 kg/ton ore)
$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	1.50 g/l (6.0 kg/ton ore)	0.75-6.00 g/l (3.0-24.0 kg/ton ore)	2.25 g/l (9.0 kg/ton ore)
$\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$	0.05 g/l (0.2 kg/ton ore)	0.05 g/l (0.2 kg/ton ore)	0.025-0.1563 g/l (0.1-0.6 kg/ton ore)

Figure 3(a) shows the zeta potential values of the ore particles suspended in the 0.001 M KCl solution in the presence of $(\text{NaPO}_3)_6$ 0.0002-0.5000 g/l. The pH of the suspension was slightly basic from 7.1 up to about 7.9 and the zeta potential of the ore particles was more negative from about -40 mV down to -74 mV. In Figure 2, the zeta potentials at the pH in this range was only about -26 mV. The results suggest that the net charge on the ore particles was more negative by the addition of $(\text{NaPO}_3)_6$.

Figure 3(b) shows the zeta potential values of the ore particles suspended in the 0.001 M HCl solution in the presence of $(\text{NaPO}_3)_6$ 0.0010 g/l and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ in the range of 0.0030-1.8750 g/l without and with an addition of $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$ 0.0005 g/l. The results confirmed the role of Na_2S as a pH regulator raising the pH of the suspension up to about 12. By addition of Na_2S , the net charge on the ore surface was more negative with the zeta potential about -110 mV, comparing to about -70 mV at the same pH in Figure 2 and also in Figure 3(a) with no $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ addition. Addition of $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$ at 0.0005 g/l had no effect on the pH of the suspension but led to a more positive zeta potential with a maximum difference of about +10 mV comparing to the case of no addition.

3.2 Infrared Spectroscopy

Figure 4(a) shows the IR spectrum from the ore confirming that it is hemimorphite type. The standard spectrum of hemimorphite phyllosilicate [7] was compared in Figure 4(b).

Three dimensional structure of hemimorphite, $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\cdot\text{H}_2\text{O}$ has been determined [8]. A projection onto (010) of the contents of two half cells bounded by $y=0$ and $y=1/2$ was given as shown in Figure 5. Surface of the ore particles in this work should be comparable to that given in the figure, containing both positive Si and Zn sites together with negative O sites.

The water absorption band (H-O-H bending) at about 1635 cm^{-1} and the O-H strong broad bands (O-H stretching) at about $3442\text{-}3436\text{ cm}^{-1}$ were observed in the spectrum from the ore. The existence of Zn-O and Si-O bonds were confirmed including the asymmetric stretching $\nu_a(\text{Si-O})$ at 1084 cm^{-1} and $1023\text{-}1020\text{ cm}^{-1}$, the $\nu_s(\text{Si-O})$ at $934\text{-}933\text{ cm}^{-1}$ and $880\text{-}875\text{ cm}^{-1}$, the Zn-O stretching vibration at $1437\text{-}1433\text{ cm}^{-1}$ and the Zn-O bending vibration at $455\text{-}470\text{ cm}^{-1}$. These absorption bands were concluded in Table 3 compared to those reported in the literatures [7,9]. Some absorption bands from additives were also observed because the aqueous solution containing these additives was recycled during the ore dressing process.

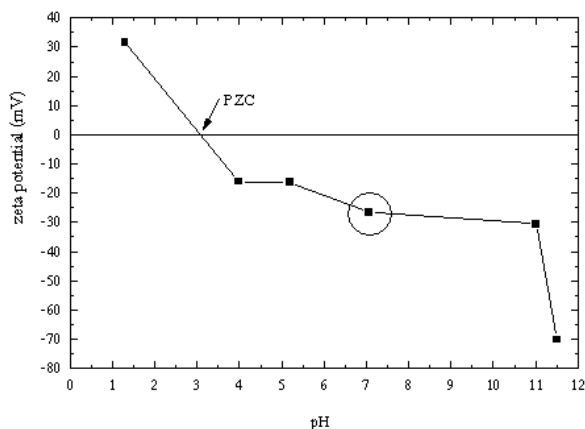


Figure 2. Zeta potential of the ore particles suspended in 0.01 M KCl solution at various pH. PZC stands for the point of zero charge.

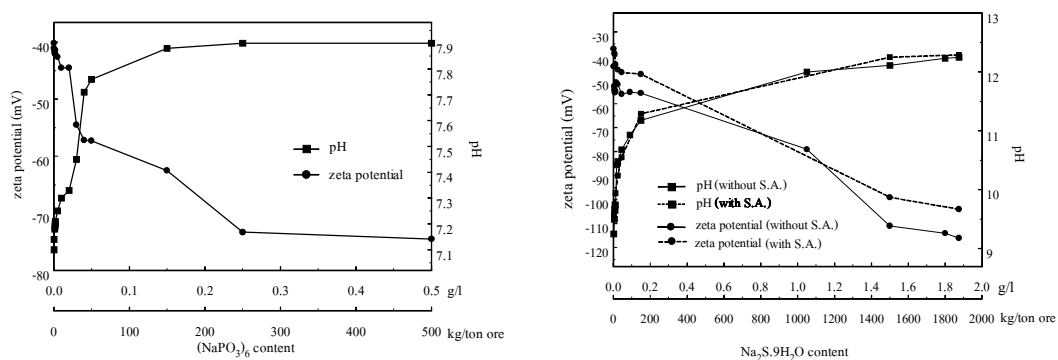


Figure 3. Effects of $(\text{NaPO}_3)_6$, Na_2S and $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$ on the zeta potential of the ore particles suspended in the 0.001 M KCl solution. S.A. denotes stearyl amine. (a) $(\text{NaPO}_3)_6$ 0.0002-0.5000 g/l and (b) $(\text{NaPO}_3)_6$ 0.0010 g/l and $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ 0.0030-1.8750 g/l without (full lines) and with (dashed lines) $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$ 0.0005 g/l.

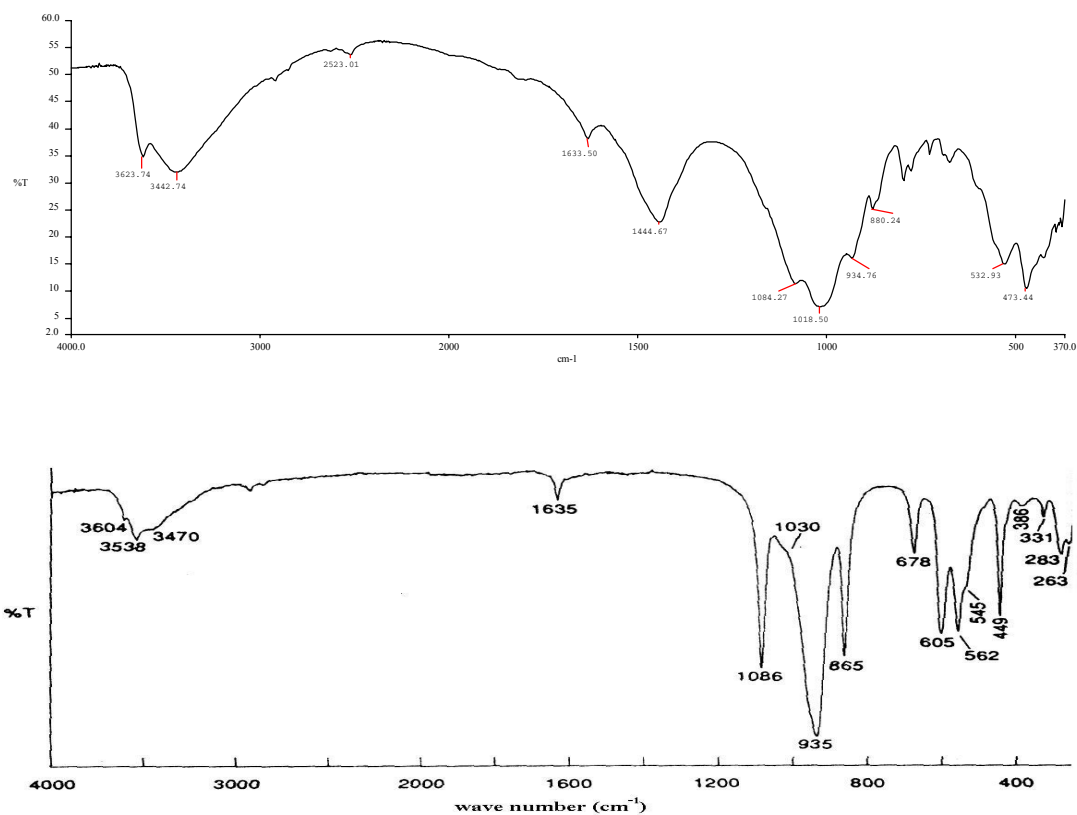


Figure 4. (a) The IR spectrum of the silicate zinc ore and (b) the standard IR spectrum from hemimorphite phyllosilicate [7].

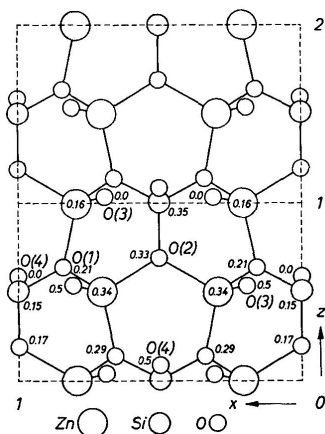


Figure 5. The structure of hemimorphite after McDonald and Cruickshank [8].

Table 3. Absorption bands which were observed in the IR spectra from the silicate zinc ore.

vibration mode	wave number from experiment (cm^{-1})	wave number from references (cm^{-1})	references
O-H stretching	3625-3623, 3441-3440	3604, 3538, 3470	[7]
H-O-H bending	1633	1635	[7]
Si-O asymmetric stretching	1084, 1023-1020	1100-1000	[7]
Si-O symmetric stretching	934-933, 880-875	900-800	[7]
Zn-O stretching	1437-1433	1475-1435	[9]
Zn-O bending	455-470	463	[9]

The IR spectra of the concentrates from the flotation experiment I (Figure 6) revealed that the hexametaphosphate anions could adsorb on both Si^{4+} and Zn^{2+} sites. The P-O stretching at $935\text{-}934\text{ cm}^{-1}$, the Na_2S position at $2525\text{-}2520\text{ cm}^{-1}$, the C-H stretching from $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$ at $2924\text{-}2923\text{ cm}^{-1}$ and the weak N-H stretching at $3443\text{-}3436\text{ cm}^{-1}$ obscured by the very strong and broad O-H stretching, were observed. A shift to the lower wave numbers of $\nu_s(\text{Si-O})$ at $880\text{-}867\text{ cm}^{-1}$ and of the Zn-O stretching at $1445\text{-}1436\text{ cm}^{-1}$ were observed, which could be attributed to the disturbance of the hexametaphosphate anions on the Si-O and Zn-O bonds. Table 4 concluded the absorption bands found in the

spectra from the concentrates comparing to those reported in the literatures [5,10-12].

From the Pearson Hard and Soft Acids and Bases theory, HSAB [13], the hexametaphosphate anions, which are strong base, should prefer to form a bond with a strong acid i.e. Si^{4+} sites lessening the Si-O bond strength. This was confirmed by a shift in the wave number to lower frequencies $\nu_s(\text{Si-O})$ at $881\text{-}867\text{ cm}^{-1}$. The higher hexametaphosphate anions content, the lower symmetric stretching frequencies were observed (Figure 6). Andreola et al. [1,14] reported a mechanism of action of sodium hexametaphosphate with the clay particles involving a chemisorption and an interaction

of hexametaphosphate anions with the exposed aluminium atoms forming complexed anions. The chemisorption produced a surface excess of negative charge and the increase of the repulsion forces

between the particles. However, sodium hexametaphosphate ring could also undergo cleavage by alkaline hydrolysis to form the corresponding linear oligophosphate [1].

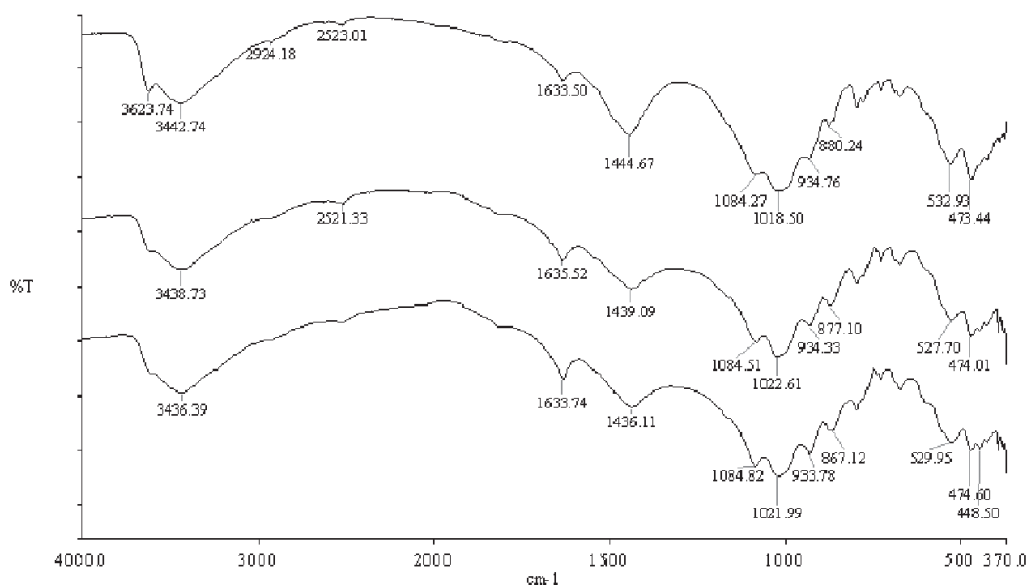


Figure 6. Infrared spectra of the concentrates from flotation experiment I. (a) $(\text{NaPO}_3)_6$ 0.0500 g/l, (b) $(\text{NaPO}_3)_6$ 0.2500 g/l and (c) $(\text{NaPO}_3)_6$ 0.4500 g/l.

The IR spectra of the concentrates from the flotation experiment II (Figure 7) revealed that the anion species from Na_2S could adsorb also on both Si^{4+} and Zn^{2+} sites. However, in this case, both the $\nu_a(\text{Si-O})$ at $1029\text{-}1008\text{ cm}^{-1}$ and $\nu_s(\text{Si-O})$ at $882\text{-}867\text{ cm}^{-1}$ were shifted to the lower wave numbers, while the single broad band Zn-O stretching at about 1439 cm^{-1} was split into three bands at $1522\text{-}1415\text{ cm}^{-1}$. The splitting of Zn-O vibrations may result from the HS^- or S^{2-} anions bound to Zn^{2+} centers and therefore lowering symmetry of the tetrahedral ZnO_4^{4-} moieties. From the Pearson Hard and Soft Acids and Bases theory, HSAB [13], the HS^- or S^{2-} anions, which are weak base from Na_2S , should prefer to form a coordinate bonding with a weak acid i.e. Zn^{2+} sites. The band at 1384 cm^{-1} could be attributed to the amine cation [5]. It has been

reported [2] that the interaction between hexametaphosphate and sodium sulphide reduced the dispersion degree in calamine zinc ores flotation. From the zeta potential measurement, anion species from Na_2S could probably replace those from $(\text{NaPO}_3)_6$ at the adsorption sites on the ore surface, leading to a more negative zeta potential and a less steric hindrance. In the pH range 8.0-11.5, HS^- could be a predominant species from sodium sulphide [2]. Salum et al. [4] reported that the dissolution of Zn^{2+} from hemimorphite and willemite into the solution was reduced when Na_2S was presented, which implied that a complex could be formed between the HS^- and the Zn^{2+} sites on the ore surface.

In the case of stearyl amine, the cationic end of the alkyl ammonium cations could have adsorbed onto the anionic sites on the ore

surface. However, no clear effect on a shift or splitting of IR absorption bands could be observed in the IR spectra of the concentrates from the flotation experiment III (Figure 8).

4. CONCLUSIONS

1. The roles of $(\text{NaPO}_3)_6$ as anionic dispersant, Na_2S as anionic sulfidiser and a pH regulator, and $\text{CH}_3(\text{CH}_2)_{17}\text{NH}_2$ as cationic collector, were confirmed by zeta potential measurement.
2. It has been recommended [15] that, to detect the surface monolayer species with bond lengths at the nanometer level by vibration spectroscopy, especially for opaque minerals, the fine particle size of about hundred angstroms should be used to increase the surface to volume ratio. Even though the particle size of the ore in this study is larger than that was recommended and the adsorbed species on the ore surface have not been detected directly, the indirect effects of the adsorbed

species on the symmetry of Si-O and Zn-O bonds on the ore surface were successfully detected as follows;

- 2.1 $(\text{NaPO}_3)_6$; a shift of $\nu_s(\text{Si-O})$ at $882\text{-}867\text{ cm}^{-1}$ and of Zn-O stretching at $1445\text{-}1436\text{ cm}^{-1}$.
- 2.2 Na_2S ; a shift of $\nu_a(\text{Si-O})$ at $1029\text{-}1008\text{ cm}^{-1}$ and $\nu_s(\text{Si-O})$ at $882\text{-}867\text{ cm}^{-1}$, a splitting of Zn-O stretching at $1522\text{-}1415\text{ cm}^{-1}$.

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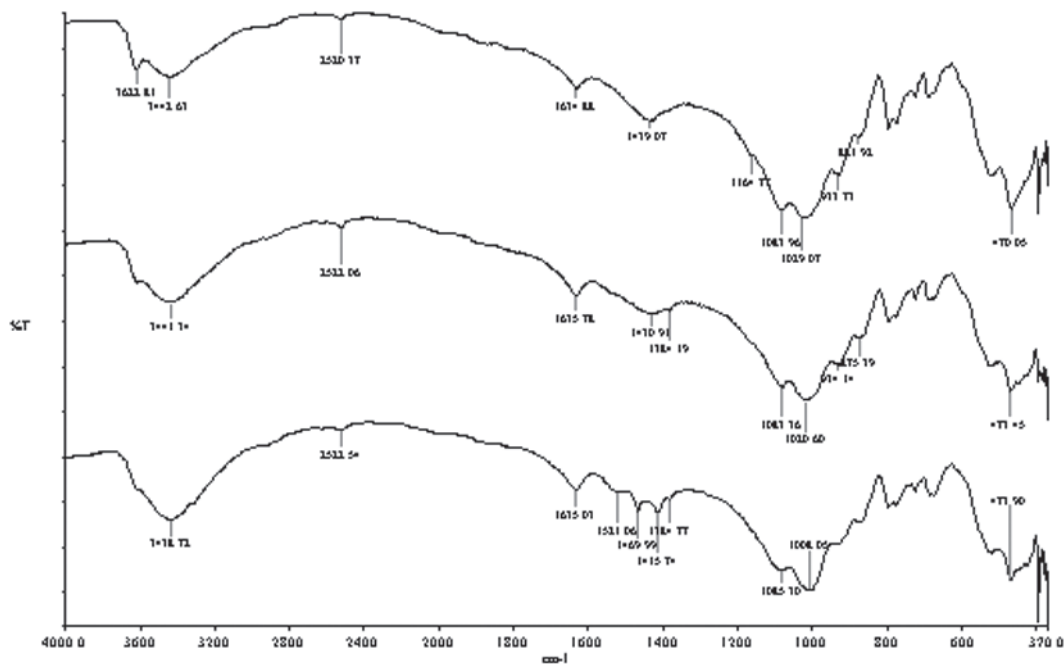


Figure 7. Infrared spectra of the concentrates from flotation experiment II. (a) $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ 0.7500 g/l, (b) $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ 2.2500 g/l and (c) $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ 4.5000 g/l.

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