doi:10.20944/preprints201811.0140.v1

Adsorption of 2-(Hexadecanoylamino)Acetic Acid Onto the Surface of Smithsonite: Mechanism and Flotation Performance

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Abstract: Zinc is mostly extracted from zinc oxide and sulfide minerals, and this process involves flotation as a key step. While it is easier to float the sulfide mineral, its consumption and depletion has led to an increased reliance on zinc oxide minerals, including smithsonite; hence the development of efficient ways of collecting smithsonite by flotation is an important objective. Herein, we describe the use of 2-(hexadecanoylamino)acetic acid (HAA), a novel surfactant, as a collector during smithsonite flotation. The mechanism and flotation performance of HAA during smithsonite flotation were investigated by total organic carbon (TOC) content studies, zeta potential measurements, FTIR spectroscopy, and XPS analyses, combined with micro-flotation experiments. The flotation results revealed that HAA is an excellent collector in pulp over a wide pH range (9–12) and at a relatively low concentration (2×10^{-4} mol/L), at which a recovery of close to 90% of the smithsonite mineral was obtained. TOC-content studies reveal that the good flotation recovery is ascribable to large amounts of collector molecule adsorbed on the smithsonite surface, while zeta potential measurements show that the HAA is chemically adsorbed onto the smithsonite. FTIR and XPS analyses reveal that the HAA-collector molecules adsorb onto the smithsonite surface as zinc-HAA complexes involving carboxylate moieties and Zn sites on the smithsonite surface in alkaline solution.

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Keywords: Smithsonite; Flotation; 2-(Hexadecanoylamino)acetic acid; Collector; Adsorption

1. Introduction

Zinc oxide and zinc sulfide ores are the primary naturally occurring zinc minerals, and these ores are mainly processed by flotation [1]. However, due to the consumption and depletion of zinc sulfide ores, oxidized zinc ores, which are more difficult to float, are being increasingly relied on. Consequently, the development of methods for the efficient processing of zinc oxide ores has become a hot research topic in recent years [2-4].

As mentioned above, the oxidized mineral is more difficult to float than the sulfide mineral, due to the greater reactivity of the surface of the oxidized mineral than that of the sulfide mineral in solution; consequently, collector molecules are unable to adsorb onto the surface of the oxidized mineral in a stable manner [5]. According to the literature, direct flotation and sulfurized flotation are the main methods used to process zinc oxide minerals. During sulfurized flotation, the oxidized zinc mineral is pre-treated with sodium sulfide, an activator, prior to flotation, which transforms the surface properties of the oxidized mineral into those of the sulfide mineral [2, 6, 7]. However, there are some problems associated with the sulfurized-flotation process, such as the lack of sulfide reactivity in the absence of Cu^{2+}, the low recovery of zinc metal obtained when xanthates are used as collectors, and the flotation foam, which is difficult to eliminate when amines are used as collectors [4, 8].

In addition, fatty acids have been used as collectors for the direct flotation of zinc oxide minerals. Fatty acids are unsatisfactory collectors for industrial use due to their low selectivities, low solubilities, and sensitivities to calcium and magnesium ions in the pulp [9]. Xanthates and amines are poor collectors for use in direct flotation; despite the zinc oxide mineral being pre-treated with a vulcanizing agent, the flotation results still do not meet our requirements [5, 10, 11]. Hence, the discovery and development of a novel and efficient collector for zinc oxide mineral flotation is urgently required.

Smithsonite, also known as zinc carbonate, is a typical zinc oxide mineral and was used as the research mineral in this study because its flotation is important to the processing of zinc. 2-(Hexadecanoylamino)acetic acid (HAA), a novel surfactant, has not been previously used to collect smithsonite during flotation; hence its flotation behavior and mechanism for adsorption onto the smithsonite surface are unknown. Therefore, it is important to study and discuss the flotation behavior and adsorption mechanism of HAA during smithsonite flotation. The mechanism and flotation performance of HAA adsorbed on the smithsonite surface were investigated by micro-flotation experiments, total organic carbon (TOC) content studies, zeta potential measurements, Fourier transform infrared (FTIR) spectroscopy, and X-ray photoelectron spectroscopy (XPS).

2. Experimental

2.1. Materials and reagents

Pure smithsonite samples used in all experiments were derived from Yunnan Province in China. Subsequently, the samples were crushed and dry ground using an agate torsion mortar. For micro-flotation tests and TOC content study, the ground product of smithsonite was sieved to achieve a particle fraction of –74+38μm using a standard screen. The rest of sample was ground to a particle fraction finer than 5μm for zeta potential measurements, FTIR and XPS analysis. The result of X-ray diffraction (XRD) pattern analysis was shown in Fig.1, which could be seen that only the diffraction peak of smithsonite was detected. It was confirmed that the smithsonite samples used in the experiments were of high purity.

AR-grade sodium chloride (NaCl), hydrochloric acid (HCl) and sodium hydroxide (NaOH) were purchased from Tianjin reagent chemical company of China. The collector HAA was purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD. Deionized water (DI water) was used in all experiments.

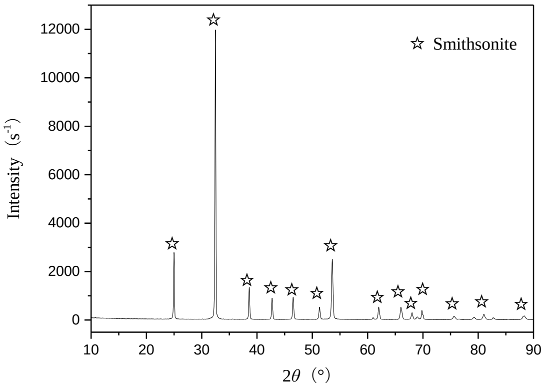


Fig. 1. X-ray diffraction pattern of the pure smithsonite sample.

2.2. Micro-flotation experiments

Micro-flotation tests were implemented under mechanical agitation in a 50mL flotation cell. 4g pure smithsonite sample was added to 40 mL solution in all experiments. HCl and NaOH were used to adjust the pulp pH. The smithsonite samples were conditioned with HAA for 3 min in required concentration and float for 3 min. After the flotation tests, the tailings and concentrates were weighed separately after filtration and drying. The recovery was calculated based on the solid mass distribution between the float products and tailings. All of the micro-flotation experiments were implemented in three times. The final experimental results show the average values.

2.3. TOC content study

4 g of smithsonite powder (–74+38µm) was introduced into 40 mL of collector solution with the desire concentration at a pH 9. After stirring for 20 min, the solution was sitting for 1 hour. Subsequently, the suspension was filtered, and the liquor samples were taken for TOC measurements with equipment HTY-DI1500. Both of the TOC amounts of the original collector solutions and treatment samples were tested to obtain the TOC reduction contribution to smithsonite adsorption. All of the samples were detected in triplicate, and the results were shown in the form of average value.

2.4. Zeta potential measurements

Zeta potential was measured in 1×10^{-3} mol/L NaCl background electrolyte solution using a zeta potential analyzer (Zetasizer Nano S90). 0.1 g of –5µm smithsonite was added to 100 mL NaCl background electrolyte solution. After stirring for 3 min at desired reagent concentration at various pH values, the pulp was sitting for 5 min. The zeta potential was measured after about 10 mL of the supernatant liquid was transferred into the measurement cell. Each sample was detection three times, and the average value as zeta potential of smithsonite.

2.5. FTIR spectrum

FTIR was conducted with an Avatar 300 from the Thermo Electron Co. The FTIR spectra in the range from 400 $cm^{-1}$to 4000 cm^{-1} were recorded. About 0.2 g of –5µm smithsonite powder was added to 100 mL collector solutions at a concentration of 3×10^{-4} mol/L. The pH of the suspension was maintained at 9 through the addition of the dilute NaOH solution during the condition. After stirring for 30 min and then sitting for 2 hours, the smithsonite sample was gently washed five times with DI water and air-dried. 50 mg of smithsonite powder was mixed with 100 mg of KBr powder in an agate. The mixture was ground to reduce the particle size and abundant mixing. The powdered mixture was then pressed into a thin plate for FTIR analysis.

2.6. XPS analysis

XPS experiments were conducted with a PHI 5000 Versa Probe II (PHI5000, ULVAC-PHI, Japan) equipped with an Al target. Smithsonite samples (-5μm) were treated with collector solution at a concentration of 3×10^{-4} mol/L. The pH of the solution was adjusted to 9. Then stirring for 30 min and sitting for 2 hours. After the adsorption achieved equilibrium, the suspension was filtered and air-dry prepared for XPS determination. Subsequently, the MultiPak Spectrum software was used to analyze the spectra and calculate surface atomic ratios of the measured samples. All the spectra were adjusted on the basis of the standard C1s binding energy (284.8 eV) and were further fitted by the Gauss–Lorentz method.

3. Results and discussion

3.1. Flotation study

Smithsonite is zinc carbonate ($ZnCO_3$), and carbonate minerals are well known to react readily under acidic conditions to consume large amounts of acid. Therefore, all experiments in this study were conducted only under natural and alkaline pH conditions. Fig. 2 displays the flotation recovery of smithsonite as a function of pulp pH (6–12) when treated with the collector at a concentration of 2×10^{-4} mol/L. The results clearly reveal that floatability increases as the pH is increased from 6 to 9; no further increases in recovery were observed at higher pH values, at which the recovery remained relatively stable. In other words, the optimal flotation recovery of smithsonite was achieved at pH 9.

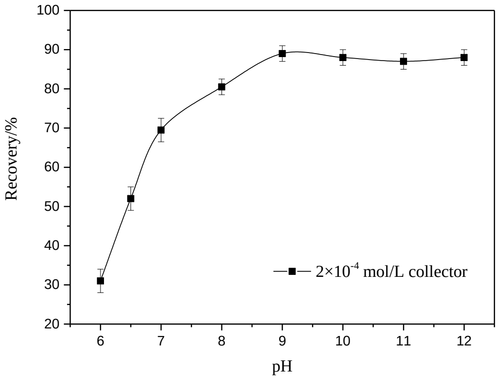


Fig. 2. Recovery of smithsonite as a function of pH.

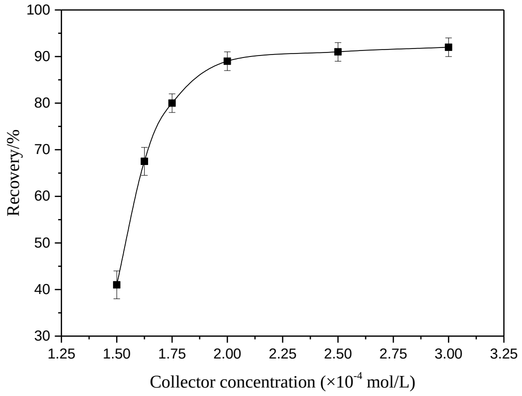


Fig. 3. Recovery of smithsonite as a function of collector concentration at pH 9.

To further know the influence of the HAA collector on smithsonite flotation, collector-concentration experiments were conducted at pH 9; Fig. 3 shows that increasing collector dosage improves smithsonite recovery. Smithsonite recovery dramatically increased as the collector concentration was variety from 1.5×10^{-4} to 2×10^{-4} mol/L; recovery was observed to increase only slightly at even higher concentrations. In particular, the flotation recovery of smithsonite exceeded 90%, which is a desired indicator, at collector concentrations in excess of 2×10^{-4} mol/L.

The above flotation analyses indicate that HAA is an excellent collector for smithsonite flotation. The floatability of smithsonite in the alkaline slurry is better than that under natural pH conditions using HAA as the collector.

3.2. HAA adsorbance on the smithsonite surface

In order to obtain more information about the adsorption state of the collector on the smithsonite surface, the amount of adsorbed collector was calculated from the difference in the TOC content of the solution before and after treatment of the smithsonite. Fig. 4 displays the TOC contents of the adsorbed collector before and after conditioning with smithsonite as functions of collector concentration. At low collector concentration, the amount of adsorbed HAA was relatively low. The adsorption of the collector increased faster as the collector concentration was increased from 1.5 × 10^{-4} to 2 × 10^{-4} mol/L. The change in TOC content was not as significant at concentrations in excess of 2 × 10^{-4} mol/L, and the amount of adsorbed collector gradually stabilized at concentrations greater than 2.5 × 10^{-4} mol/L. This trend is consistent with the results from the flotation experiments. The excellent floatability of smithsonite is attributable to large amounts of collector molecule adsorbed onto the smithsonite surface.

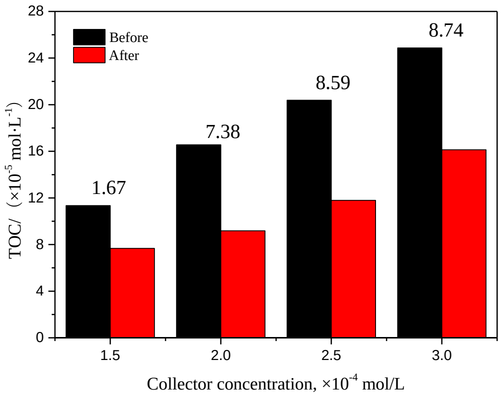


Fig. 4. Reduction in the TOC content (the amount is noted above each column) of the collector solution as a function of collector concentration at pH 9.

3.3. Effect of HAA on the zeta potential of smithsonite

Samples of smithsonite powder were placed in a zeta-potential cell, either in the absence or presence of the collector. Following instrument calibration, the zeta potential of the smithsonite sample was determined in order to provide information on the collector-ion species in the pulp suspension that are adsorbed on the smithsonite surface.

Smithsonite is a semi-soluble salt mineral; it has a solubility product constant of 1.46×10^{-10} M. The main characteristics of a salt mineral are ionic bonding and moderate water solubility [11, 12]. The dissolution of smithsonite in solution is described as follows:

$$ZnCO_3 = Zn^{2+} + CO_3^{2-} \qquad (1)$$

In the flotation system, water molecules chemically adsorb onto the smithsonite surface with increasing smithsonite surface activity in water. Compared to zinc sulfide minerals, the main factor responsible for the low natural floatability of smithsonite is the high activity of water dipoles. This phenomenon decreases the probability of effective reagent adsorption on the smithsonite surface [13, 14]. The chemistry of smithsonite dissolution and hydrolysis reactions involving Zn^{2+}, together with equilibrium constants in open solutions, are shown in Table 1 [5, 15, 16].

Table 1

Pertinent reactions and thermodynamic data of smithsonite dissolution in the open solution.

Pertinent reactions and constant			Pertinent reactions and constant		
(2)	$CO_3^{2-}+H^+\Leftrightarrow HCO_3^-$	10.33	(10)	$Zn^{2+}+4OH^-\Leftrightarrow Zn(OH)_4^{2-}$	14.80
(3)	$CO_2(g)+OH^-\Leftrightarrow HCO_3^-$	6.18	(11)	$Zn^{2+}+HCO_3^-\Leftrightarrow ZnHCO_3^+$	2.10
(4)	$OH^-+H^+\Leftrightarrow H_2O$	14.00	(12)	$Zn^{2+}+CO_3^{2-}\Leftrightarrow ZnCO_3$	5.30
(5)	$HCO_3^-+H^+\Leftrightarrow H_2CO_3$	6.35	(13)	$Zn^{2+}+2CO_3^{2-}\Leftrightarrow Zn(CO_3)_2^{2-}$	9.63
(6)	$Zn^{2+}+OH^-\Leftrightarrow ZnOH^+$	5.00	(14)	$Zn^{2+}+CO_3^{2-}\Leftrightarrow ZnCO_3(s)$	10.00

(7)	$Zn^{2+}+2OH^{-}\Leftrightarrow Zn(OH)_2(aq)$	11.10	(15)	$Zn(OH)_2(s)+2H^{+}\Leftrightarrow Zn^{2+}+2H_2O$	11.50
(8)	$Zn^{2+}+3OH^{-}\Leftrightarrow Zn(OH)_3^{-}$	13.60			
(9)	$Zn(CO_3)_{0.4}(OH)_{1.2}\Leftrightarrow Zn^{2+}+0.4CO_3^{2-}+1.2OH^{-}$	14.85			

Table 1 reveals that a complex mixture of species is formed when smithsonite is dissolved in water. Some studies have shown that $\equiv ZnOH^0$ and $\equiv CO_3H^0$ (where "≡" represents the surface) are the two primary hydration sites that govern surface speciation [15, 16]. There is a large amount of experimental evidence indicating that complex reactions occur on the surface of smithsonite. According to the literature, some of the reactions that occur on the surface of smithsonite depend on the solution conditions; these reactions are described as follows [17-19]:

$\equiv CO3H^0 \Leftrightarrow \equiv CO3^{-} + H^{+}$ (16)

$\equiv CO3H^0 + Zn^{2+} \Leftrightarrow \equiv CO_3Zn^{+} + H^{+}$ (17)

$\equiv CO_3H^0 + ZnOH^{+} \Leftrightarrow \equiv CO_3ZnOH^0 + H^{+}$ (18)

$\equiv ZnOH^0 + H^{+} \Leftrightarrow \equiv ZnOH_2^{+}$ (19)

$\equiv ZnOH^0 \Leftrightarrow \equiv ZnO^{-} +H^{+}$ (20)

$\equiv ZnOH^0 + HCO_3^{-} + H^{+} \Leftrightarrow \equiv ZnHCO_3^0 + H_2O$ (21)

$\equiv ZnOH^0 + CO_3^{2-} + H^{+} \Leftrightarrow \equiv ZnCO_3^{-} + H_2O$ (22)

As is evident from the above, the smithsonite surface is charged through non-stoichiometric dissolution and hydrolysis, with some ions released into the solution. The Zn^{2+} hydrolysis products then readsorb onto the smithsonite surface. The smithsonite-surface charge is also determined by interactions between ions in its crystal structure and the hydrolysis products. Some ions (Zn^{2+}, HCO_3^{-}, H^{+}, OH^{-}, and CO_3^{2-}) determine the potential between the smithsonite surface and the solution, and deprotonation and protonation reactions determine the charge of the smithsonite surface; these reactions depend on the solution conditions.

Fig. 5 displays the zeta potentials of smithsonite in the absence and presence of the collector as functions of pH. The zeta potential of pure smithsonite became more negative with increasing pH, which is consistent with the findings of former investigations [4, 20]. The isoelectric point (IEP) of smithsonite has been reported to lie between pH 7 and 8.8 [5, 18]. As is evident from Fig. 5, the IEP of pure smithsonite in the absence of the collector is approximately pH 7.6, which is in agreement with the results of previous studies. The zeta potential of smithsonite rapidly declines at pH values above 7.6.

The change in the potential of the surface of pure smithsonite has previously been described in the following way [2, 4, 5, 17, 18]: The increasing zeta potential of pure smithsonite (Fig. 5), from 0 mV at pH 7.6, to 15.80 mV at pH 6, is ascribable to the chemical adsorption of protons and Zn^{2+} according to reactions 16 and 17, which result in increasing concentrations of Zn^{2+} and hydrogen ions in solution with decreasing pH, and the smithsonite dissolves as a consequence. According to the distributions of species in previous studies, the concentration of Zn^{2+} increases faster than that of hydrogen ions. At the same time, the $\equiv ZnOH_2^+$ site on the mineral surface (reaction 19) is formed by the protonation of $\equiv ZnOH^0$ [21, 22]. As the solution pH is increased from 7.6 to 9, the zeta potential reveals that the smithsonite becomes negatively charge due to the deprotonation of $\equiv ZnOH_2^+$, and two sites ($\equiv ZnHCO_3^0$ and $\equiv ZnCO_3^-$) are formed through the chemical adsorption of HCO_3^- and CO_3^{2-} (reactions 21 and 22) [5]. Meanwhile, the chemical adsorption of $ZnOH^+$ is possible at the $\equiv CO_3H^0$ site (reaction 18) [23, 24]. At pH > 9, the slope of the zeta-potential curve for pure smithsonite gradually flattened, as opposed to the curve at 7.6 < pH < 9， which indicates that the hydrolysis products may have readsorbed onto the mineral surface, resulting in a more negative zeta potential at pH greater than 9. According to previous investigations, the ≡ZnO⁻ species are dominant in solution at pH > 12, which confirms that reaction 20 rarely takes place under these solution conditions.

Fig. 5 reveals that the zeta potential of smithsonite becomes more negative in the collector solution compared to that of pure smithsonite. Furthermore, higher collector concentrations lead to more negative charge on the mineral surface. The HAA collector may ionize to form an anionic collector in solution due to the presence of the carboxylic acid group in the HAA molecule; the increase in the degree of ionization would be expected to follow the rise in solution alkalinity. Therefore, the anionic collector molecules are absorbed onto the mineral surface, resulting in a decrease in the zeta potential of smithsonite in the 6–12 pH range. All of these experiments showed that the zeta potentials were more negative that those obtained in DI water, in which collector ions are unable to physically adsorb onto the mineral surface due to electrostatic repulsion. Therefore, the collector becomes chemisorbed onto the mineral surface.

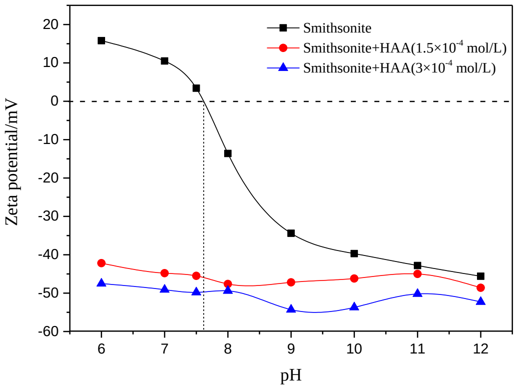


Fig. 5. Zeta potential of smithsonite as a function of pH after conditioning with DI water and the collector.

3.4. FTIR analyses

In order to gain further insight into the adsorption state of the collector on the mineral surface, we subjected the HAA collector, before and after absorption by smithsonite, to FTIR spectroscopy, the results of which are shown in Fig. 6.

Spectrum (a) is that of HAA in the 500–4000 cm^{-1} range; this spectrum exhibits peaks at 3327 cm^{-1} due to the stretching vibrations of the N-H bond, at 2918 cm^{-1} and 2849 cm^{-1} that correspond to the C-H stretches of -CH_3 and -CH_2 units, and 1703 cm^{-1}, which is assigned to the C=O bond of the carboxylic acid moiety in the collector molecule [25, 26]. The peaks at 1645 cm^{-1} and 1559 cm^{-1} are assigned to amide I and II vibrations; amide I arises from the C=O stretch, while the amide II band is mostly due to N–H and C–H vibrations [27-30], while peaks that appear at 1472 cm^{-1} and 719 cm^{-1} are representative of C-H bending, and C-N and C-O stretching bands are observed at 1272 cm^{-1} and 1037 cm^{-1}, respectively [31-33]. In addition, spectra (b) and (c) belong to smithsonite samples treated with DI water and the HAA collector, respectively. Spectrum (b) exhibits three strong peaks at 1428 cm^{-1}, 870 cm^{-1}, and 743 cm^{-1}, which are characteristic smithsonite bands that correspond to the asymmetric stretching (C-O) and bending (C-O-C) vibrations of CO_3^{2-}, respectively [34, 35]. Meanwhile, the obvious peak at 3448 cm^{-1} is attributed to the O-H stretching vibrations of the water molecule present on the mineral surface as a consequence of exposure to DI water [32, 36]. Compared to spectrum (b), some new peaks are observed in the spectrum (c) of the smithsonite sample following collector treatment, namely new peaks at 2918 cm^{-1} and 2849 cm^{-1} that correspond to hydrocarbon chains (-CH_3 and -CH_2 bond), 1617 cm^{-1} (C=O bond in amide), and 1558 cm^{-1} (N–H bond in amide). The broad peak observed at 3435 cm^{-1} in spectrum (c) is due to overlapping N-H and O-H stretching peaks following collector treatment. Meanwhile, the peak at 1703 cm^{-1} disappeared upon collector treatment; its disappearance, and the rise of peaks at 3435 cm^{-1}, 1617 cm^{-1}, and 1558 cm^{-1} are further evidence that chemical adsorption on the smithsonite surface occurs through Zn sites that react with carboxyl groups of HAA molecules. The characteristic peaks for the C-O-C and C-O in CO_3^{2-} units of smithsonite following absorption of the HAA collector did not significantly shift from their positions prior to treatment, which confirms that the CO_3^{2-} groups do not participate in the chemical reaction.

These FTIR analyses indicate that the HAA collector was successfully adsorbed by the smithsonite, most likely through interactions of its carboxyl group with Zn sites on the smithsonite surface in weakly alkaline solutions, possibly through the formation of covalent bonds.

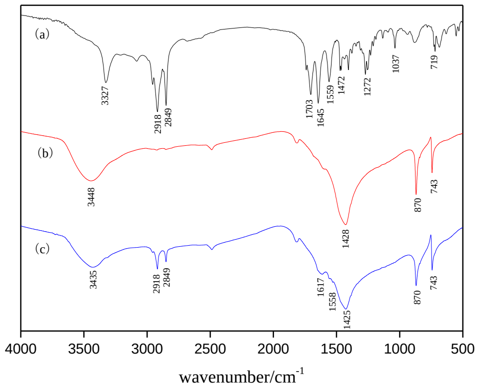


Fig. 6. FTIR spectra of (a) the HAA-collector, and (b, c) smithsonite before and after treatment with HAA (concentration: 5×10^{-4} mol/L) at pH 9, respectively.

3.5. XPS analyses

In order to confirm the interpretation of the FTIR spectra and to further understand the adsorption state of the smithsonite surface during flotation, we examined smithsonite samples before and after treatment with HAA by XPS. The C1s, O1s, Zn2p, and N1s binding energies were then determined by spectral peak fitting, and the MultiPak Spectrum software was used to calculate the relative concentrations of the various elements on the smithsonite surface in the absence and presence of the collector. Fig. 7 displays the XPS spectra processed by the MultiPak

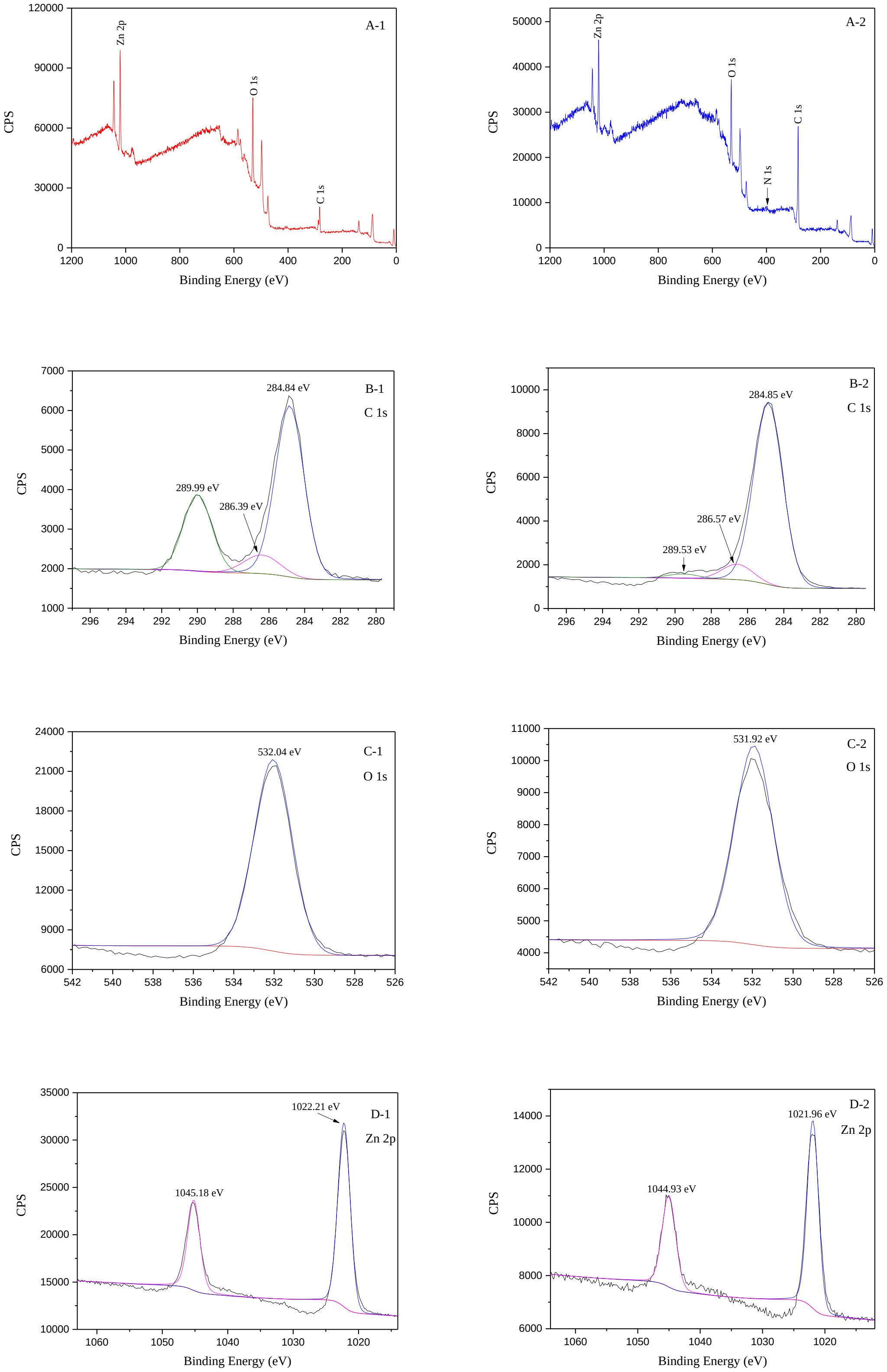
Spectrum software. Panels A-1, B-1, C-1, and D-1 in Fig. 7 show the XPS spectra of a pure smithsonite sample treated with DI water; panel A-1 shows the full spectrum, while the C1s, O1s, and Zn2p spectra are displayed in panels B-1, C-1, and D-1, respectively. Panels A-2, B-2, C-2, and D-2 in Fig. 7 are the corresponding spectra of the smithsonite samples treated with the HAA collector, while panel E-2 shows the N1s spectrum of smithsonite following collector adsorption.

Panel A-1 in Fig. 7 reveals that only elemental C, O, and Zn were detected in the full XPS spectrum of pure smithsonite treated with DI water, which shows that the smithsonite samples used in these experiments were of high purity. Compared to panel A-1, a N signal was observed in the XPS spectrum (panel A-2) after the smithsonite sample was treated with the collector, which is consistent with adsorption of the collector onto the smithsonite surface. Table 2 provides a semi-quantitative summary of the atomic concentrations of the smithsonite surface before and after treatment with the collector. The carbon concentration was observed to increase from 42.38% to 69.59%, while the oxygen concentration decreased from 39.08% to 24.40%, and the zinc concentration decreased from 15.53% to 7.38%. At the same time, nitrogen, at a level of 2.97% emerged on the mineral surface following treatment with the collector. These changes in atomic concentrations are further evidence that the collector was adsorbed onto the mineral surface.

In panel B-1, the two C1s peaks, at 286.39 eV and 289.99 eV, correspond to C-O and C=O bonds assigned to the carbon in the carbonate group of smithsonite samples[35, 37], while the other peak at 284.84 eV is attributed to C-C and C-H contaminants [2]. A 0.18 eV shift in the C-O-bond peak, and a 0.46 eV change in the energy of the C=O bonds in the carbonate groups shown in panel B-2 are attributed to collector adsorption. At the same time, the binding energy at

289.53 eV shown in panel B-2 is attributed to the C=O bond in carboxylic group of the collector and carbonate groups [35]. In other words, only the C1s peaks at 289.99, 286.39, 289.53, and 286.57 eV are derived from the smithsonite sample; the remaining C1s binding energies are not assigned to the surface composition of pure smithsonite. In panel C-1, the O1s binding energy at 532.04 eV corresponds to the O in the C-O and C=O bonds of the carbonate group [35, 38]. The O1s binding energy shifted from 532.04 eV to 531.92 eV following collector adsorption onto the smithsonite surface. In panel D-1, the two peaks at 1045.18 eV and 1022.21 eV in the spectrum of the untreated smithsonite sample correspond to $Zn2p_{1/2}$ and $Zn2p_{2/3}$ binding energies, and are consistent with previous reports [2, 16, 35, 38, 39]. Following collector adsorption onto the smithsonite, the $Zn2p_{1/2}$ binding energy was observed to shift to 1044.93 eV, while the $Zn2p_{2/3}$ energy moved to 1021.96 eV; these 0.25 eV differences are attributable to Zn-O bond formation according to previous studies [35], which is consistent with chemical adsorption of the collector at the Zn sites on the smithsonite surface. The carboxylic acid is deprotonated in alkaline solution. The formation of Zn-O bonds, and the structure of the collector suggest that Zn-O bonds are formed through reactions of the Zn sites on the smithsonite surface and the carboxylates of deprotonated collector molecules. According to former studies, the first N1s peak at 399.60 eV (panel E-2) is attributed to the amino group of the HAA collector [40].

In a word, changes in the O1s, Zn2p, and N1s binding energies indicate that the HAA collector is chemically adsorbed onto the smithsonite surface. According to the XPS results, the HAA collector is adsorbed onto the smithsonite surface through Zn sites that react with the carboxylate of the deprotonated HAA to form covalent bonds, which is consistent with the FTIR observations. In other words, the collector molecules are adsorbed on the smithsonite surface as zinc-HAA complexes. The proposed adsorption of the HAA molecule onto the smithsonite surface is shown Fig. 8.



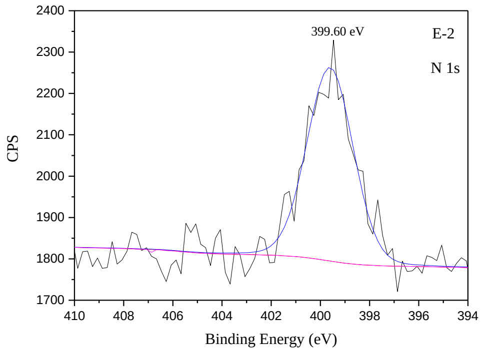


Fig. 7. XPS spectra of smithsonite treated with DI water (left) the and collector (right, concentration of 5×10^{-4} mol/L) at pH 9.

Table 2 The results of atomic concentration on smithsonite surface by semi-quantitative analysis.

Samples	Atomic concentration, %			
	C1s	O1s	Zn2p	N1s
Raw material	42.38	39.08	15.53	
collector adsorption	69.59	24.40	7.38	2.97

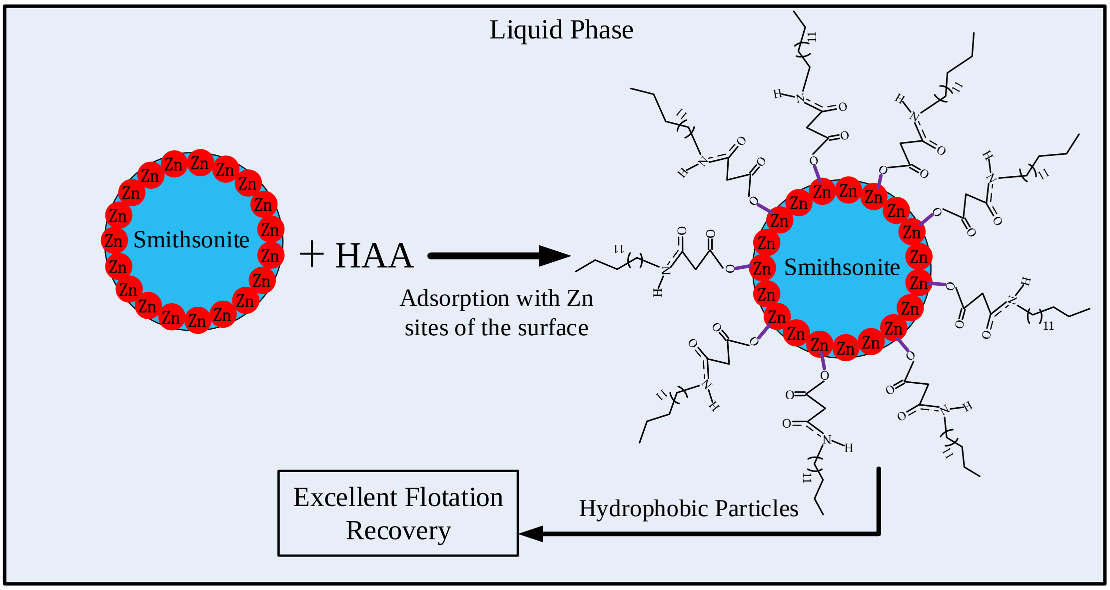


Fig. 8. Depicting the proposed process for the adsorption of HAA molecules on the smithsonite surface.

4. Conclusions

The HAA surfactant was used for the first time as a collector for smithsonite flotation. HAA exhibited excellent collecting performance as evidenced by micro-flotation experiments and TOC-content studies. The flotation recovery of pure smithsonite was 90% at a collector concentration of 2×10^{-4} mol/L over a wide range of pulp pH values (9–12). According to the TOC-content studies, the good flotation recovery is ascribable to large amounts of collector molecule adsorbed on the smithsonite surface.

Zeta potential measurements revealed that the HAA is chemically adsorbed onto the smithsonite. The disappearance of the carboxyl peak in the FTIR spectrum, and the observed shift in the position of the C=O peak of the amide group indicate that HAA was successfully adsorbed onto the smithsonite surface, most likely through reactions of carboxylate moieties with Zn sites on the smithsonite surface. XPS further revealed that the HAA collector was adsorbed on the smithsonite surface through the formation of covalently bound zinc-HAA complexes, in which HAA molecules interact with Zn sites on the smithsonite surface.

Acknowledgements

The research project was finance support provided by the National Natural Science Foundation of China (No.51764021) and the Analysis and Testing Foundation of Kunming University of Science and Technology (No.2017M20152201097).

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