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Hemimorphite Flotation with 1-Hydroxydodecylidene-1,1-diphosphonic Acid and Its Mechanism

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Abstract: 1-hydroxydodecylidene-1,1-diphosphonic acid (HDDPA) was prepared and first applied in flotation of hemimorphite. HDDPA exhibited superior flotation performances for recovery of hemimorphite in comparison with lauric acid, and it also possessed good selectivity against quartz flotation under pH 7.0–11.0. Contact angle results revealed that HDDPA preferred to attach on hemimorphite rather than quartz and promoted the hydrophobicity of hemimorphite surfaces. In the presence of HDDPA anions, the zeta potential of hemimorphite particles shifted to more negative value even if hemimorphite was negatively charged, inferring a strong chemisorption of hemimorphite to HDDPA. The Fourier transform infrared (FTIR) recommended that HDDPA might anchor on hemimorphite surfaces through bonding the oxygen atoms of its P(=O)–O groups with surface Zn(II) atoms. X-ray photoelectron spectroscopy (XPS) gave additional evidence that the Zn(II)-HDDPA surface complexes were formed on hemimorphite.

Keywords: 1-hydroxydodecylidene-1,1-diphosphonic acid; hemimorphite; flotation; hydrophobic mechanism.

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1. Introduction

The adsorption of surfactants on to material particles can modify their surface properties such as surface energy, surface charge and hydrophobicity. These changes are prerequisites to froth flotation, which is the most principal process for enrichment and separation of value minerals from their ores [1–5]. In froth flotation, a collector (one kind of surfactant) selectively attaches to a target mineral using its minerophilic group, and then its hydrophobic group attaches to air/nitrogen bubbles which delivers the mineral particles to the slurry interface [6,7].

In general, zinc oxide minerals such as hemimorphite ($Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$), smithsonite ($ZnCO_3$), willemite ($Zn_2SiO_4$) and hydrozincite ($Zn_5(CO_3)_2(OH)_6$) exhibit good hydrophilicity and unsatisfactory floatability. According to the predominant zinc oxide minerals, the ore varieties of zinc oxide are divided into hemimorphite, smithsonite and willemite + hemimorphite, and quartz is of the main gangue mineral for the three basic ore types [8].

Zinc oxide ores are much more difficult to be recovered by froth flotation than zinc sulfide ores which are becoming depleted due to continuous exploitation [9,10]. Zinc oxide minerals are commonly floated by amine collectors after presulfidization with sulfurizing agents like Na_2S, NaHS or NH_4HS [11]. Xanthates and the mixture of amines and xanthates also exhibit suitable performance for beneficiation of zinc oxide minerals [12,13]. However, it is tough to accurately control the dose of sulfidizing agents, which has a significant influence on presulfidization effects, pulp pH and then on zinc flotation recovery [14,15]. The application of fatty acid collectors can wipe out the presulfidization process [13]. It also faces flaws such as high operational costs and weak selectivity for gangue minerals [14]. Mercaptan surfactants might be selective collectors for flotation of zinc oxide minerals. They also suffer from high consumption and foul odor [13,16].

Chelating collectors, such as salicylaldoxime, 8-hydroxyquinoline and amino-thio-phenol (ATP), can exert chelating action towards Zn atoms and possess good selectivity to beneficiate zinc oxide minerals [13,17]. Therefore, the flotation of zinc oxide minerals by chelating agents might be a promising approach [18,19].

Because of their favorable chelating nature for Zn, Cu, Sn, Ti and Cd ions, phosphorous acid surfactants have been selected as flotation collectors for recovery of metal oxide minerals [20–23]. Styryl phosphonic acid (SPA) has been recommended as a selective collector for enrichment of the finely disseminated rutile and cassiterite [24,25]. α-Hydroxyl octyl phosphinic acid (HPA) exhibited good flotation response to ilmenite, cassiterite or malachite [26–29].

1-Hydroxyalkylidene-1,1-diphosphonic acid (HADPA), as an extensively investigated chelating agent for extraction of metal ions, is able to form stable metal chelation with zinc, manganese, copper, lead, calcium, nickel or cobalt. Among these complexes, its zinc complexes might be the most stable [30,31]. HADPA surfactants have been chosen as collectors for flotation of phosphate, fluorite, tin, tungsten and oxidized sulfide ores [32,33]. The flotation reagent Flotol-7,9, mainly containing HADPA with 7–9 carbon atoms, was used as a commercial collector by Kotlyarevsky et al. [32], they found that Flotol-7,9 was very effective for fluorite flotation from silicate-fluorite ores. However, the fatty acid collectors did not achieve good separation efficiency in flotation of these ores. Additionally, Flotol-7,9 exhibited better selectivity for cassiterite flotation than *p*-tolylarsonic acid, SPA, alkyl hydroxamic acids with 7–9 carbon atoms and tetrasodium salt of *N*-octadecyl-*N*-sulphosuccinoyl aspartic acid [32]. Flotol-7,9 can selectively separate apatite from brazilite-apatite-magnetite ores by froth flotation and formed calcium acid orthophosphates on apatite surfaces [32,34]. Pradip and Chaudhari [35] considered HADPA possessed strong chelating properties toward tungsten and exhibited better selectivity for flotation of wolframite than sodium oleate. Chen et al. [36] thought that 1-hydroxyoctylidene-1,1-diphosphonic acid was an effective collector for niobite flotation with good selectivity, and it chemisorbed on to niobite surfaces through its –P=O and –P–O– group. Zheng et al. [37] also found that 1-hydroxyoctylidene-1,1-diphosphonic acid chemisorbed on to the synthesized fersmite surfaces through its –P=O and –P–O– group. Nevertheless, HADPA has been hardly reported as a collector for flotation recovery of zinc oxide minerals in the published literature.

For the excellent affinity to zinc ions [30,31], a novel HADPA surfactant, 1-hydroxydodecylidene-1,1-diphosphonic acid (HDDPA) was selected as a collector for hemimorphite flotation. The flotation response of HDDPA to hemimorphite and quartz was investigated by micro-flotation experiments on single and artificially mixed minerals. After that, zeta potential, contact angle, Fourier transform infrared (FTIR) and X-ray photoelectron spectroscopy (XPS) were adopted to evaluate the hydrophobic mechanism of HDDPA on hemimorphite/water interface.

2. Materials and Methods

2.1. Materials

HDDPA was prepared and purified in our laboratory, and characterized by and ^{1}H and ^{31}P NMR. Other chemicals used in this research were analytical grade (AR) from commercial suppliers. Distilled H_2O was used in this research unless elsewise asserted. The X-ray diffraction (XRD) pattern and X-ray fluorescence (XRF) of hemimorphite and quartz samples were separately listed in Figure 1 and Table 1, which show that the purity of the two minerals was over 98%. The fraction with particle size ranging from +37 to -74 μm was employed for the micro-flotation tests and that below 5 μm was selected for the zeta potential, FTIR and XPS measurements. The specific surface area of the +37 to -74 μm portion was determined as 0.76 for hemimorphite and 0.12 $m^2 \cdot g^{-1}$ for quartz via the Brunauer-Emmett-Teller method on the Nova1000 analyzer (Quantachrome Instru., Boynton Beach, FL, USA).

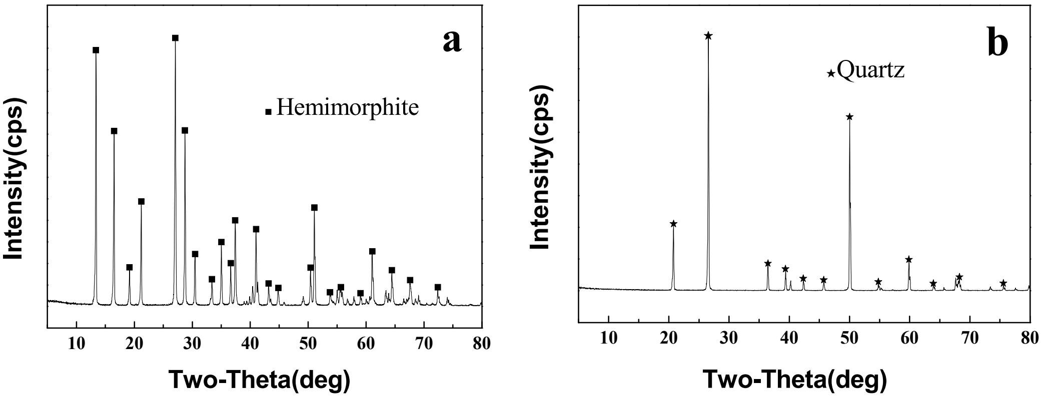

Figure 1. X-ray Diffraction (XRD) of hemimorphite (**a**) and quartz (**b**) samples.

Table 1. The element content of hemimorphite and quartz by X-ray fluorescence (XRF) (wt %).

Composition	Zn	O	Si	Mg	Ca	Cu	P	Cl	S	Fe	Pb	Al
Hemimorphite	57.53	31.00	10.92	0.218	0.115	0.08	0.04	0.01	0.02	0.01	0.02	-
Quartz	-	56.20	43.60	0.06	0.04	-	-	-	-	0.02	-	0.07

2.2. Micro-Flotation Tests

Micro-flotation tests were carried out in an improved Hallimond tube. For each experiment, 180 mL water and 2 g of mineral samples were placed into a 400-mL beaker. After regulating the pulp pH to a designed value by dilute NaOH or HCl solutions, collector (HDDPA or lauric acid), frother MIBC (methyl isobutyl carbinol), and extra H_2O were put in to obtain a 220 mL suspension where MIBC concentration was 1.5×10^{-4} mol·L^{-1}. The pulp was stirred for 3 min and its pH values were detected. Later, the suspension was siphoned into the Hallimond tube and the micro-flotation was performed for 3 min under 0.2 L·min^{-1} of N_2. The froth or tailings products were filtered, dried and weighted. The recovery was computed according to the products obtained as listed in Equation (1) for pure mineral, Equation (2) for hemimorphite and Equation (3) for quartz in the artificially mixed minerals, respectively.

$$\varepsilon = \frac{\mathrm{m}_1}{\mathrm{m}_1+\mathrm{m}_2} \times 100\% \tag{1}$$

$$\varepsilon_{\mathrm{Hemimorphite}} = \frac{\mathrm{m}_1 \times \beta_1}{\mathrm{m}_1 \times \beta_1 + \mathrm{m}_2 \times \beta_2} \times 100\% \tag{2}$$

$$\varepsilon_{\mathrm{Quartz}} = \frac{\mathrm{m}_1 - \mathrm{m}_1 \times \beta_1}{\mathrm{m}_1 + \mathrm{m}_2 - \mathrm{m}_1 \times \beta_1 - \mathrm{m}_2 \times \beta_2} \times 100\% \tag{3}$$

where ε is the recovery of hemimorphite or quartz, m_1 and m_2 are the weight of froth products and tailings (g), β_1 and β_2 are the hemimorphite content of the froth products and tailings (%, *w*/*w*), respectively. The presented recovery was the average value of two independent flotation tests.

2.3. Zeta Potential Measurement

The zeta potential of hemimorphite or quartz in the presence or absence of HDDPA was measured in 1×10^{-2} mol·L^{-1} KNO_3 by using the ZetaPlus zeta potential analyzer (Brookhaven, NY, USA). In each test, 50 mg of hemimorphite or quartz samples were introduced into 40 mL KNO_3 solutions. After adjusting the suspension pH with dilute HNO_3 or KOH solutions, extra KNO_3 solutions with or without HDDPA were added to obtain the 50 mL slurry. The suspension with or without 2×10^{-4} mol·L^{-1} HDDPA was agitated for 10 min, then, its zeta-potential and pH values were measured. The reported zeta potential was the average value of six independent measurements with ±5 mV variation.

2.4. Contact Angle Measurements

The contact angles of hemimorphite or quartz surfaces before and after HDDPA modification were measured by using the water droplet captive method on the JC2000C contact angle instrument (Zhongchen Digital, Shanghai, China). The chunk samples were successively wet-polished by hand with SiC abrasive papers, and 1 and 0.05 µm Al_2O_3 powder suspensions. After cleaning several times with distilled H_2O under ultrasound, the mineral samples were dried by pure N_2 and applied for contact angle measurements. The results reported were the average value of five measurements.

2.5. FTIR Measurement

When 2×10^{-4} mol·L^{-1} HDDPA solutions were mixed with 2×10^{-4} mol·L^{-1} Zn^{2+} aqueous solutions with a volume ratio of 1:8, a white precipitate emerged. The precipitates in the mixture were filtrated, rinsed four times with distilled H_2O, and then desiccated in a vacuum oven. 0.5 g of 5 µm hemimorphite particles were put into 100 mL of 5×10^{-4} mol·L^{-1} HDDPA, which was agitated for 4 h at 298 ± 1 K. After filtrating, washing thrice with H_2O and drying, the hemimorphite particles adsorbed HDDPA were applied for FTIR detection on the 740 FTIR instrument (Nicolet, Glendale, WI, USA) through KBr disks.

2.6. XPS Measurement

The XPS of HDDPA, hemimorphite before and after HDDPA adsorption, and Zn-HDDPA precipitates were measured on the ESCALAB 250Xi (Thermo Scientific, Waltham, MA, USA) using Al Kα X-ray source conducted at 200 W with 20 eV pass energy. The vacuum pressure was between 10^{-9} to 10^{-8} Torr and the takeoff angle was set at 45°.

3. Results

3.1. Preparation of HDDPA

HDDPA was prepared according to the method reported by Kieczykowski et al. [38]. Lauric acid (20 g, 0.1 mol), phosphorus acid (8.2 g, 0.1 mol) and methanesulfonic acid (20 mL) were put in a three-necked bottle equipped with a reflux condenser and a $CaCl_2$-tube. After heating the mixture to 65 °C, PCl_3 (13 mL, 0.146 mol) was introduced dropwise and the reactive mixture was agitated at 70 °C for 18 h. Then, the mixture was cooled, 20 mL CH_3CH_2OH (EtOH) was added to separate methanesulfonic acid (with a near 80% recovery), and 50 mL H_2O was put into the mixture which was agitated under reflux for 5 h. After cooling the solution to 20 °C, the pH was adjusted to around 1.0 with NaOH to precipitate HDDPA which was filtrated, washed with EtOH and collected as white solid with 97% yield.

Characterization of HDDPA: ^{1}H-NMR (500 MHz, D_2O/NaOD, Bruker AvanceIII, Bruker, Uster, Switzerland), δ (ppm): 1.83–1.71 (m, 2H), 1.45 (m, 2H), 1.19 (s, 16H), 0.77 (t, 3H). ^{31}P NMR(202 MHz, D_2O/NaOD), δ (ppm): 19.01. FTIR (KBr), v (cm^{-1}): 3540, 3446, 3228, 2960, 2920, 2850, 2240, 1470, 1290, 1160, 1060, 922, 721, 667, 596, 544.

3.2. Micro-Flotation Results

The effect of pH or collector concentration on the flotation recovery of hemimorphite or quartz is presented in Figure 2. The results in Figure 2a,c indicated that under pH 7.0–11.0, HDDPA achieved higher flotation recovery of hemimorphite and exhibited better flotation selectivity against quartz than lauric acid. The results in Figure 2b,d showed that the flotation recovery of hemimorphite increased with an increase of collector dose, and 1×10^{-4} mol·L^{-1} HDDPA recovered near 85.2% hemimorphite or 29.4% quartz, while the recoveries of hemimorphite and quartz were 72.3% and 51.6% by using 1×10^{-4} mol/L lauric acid, respectively.

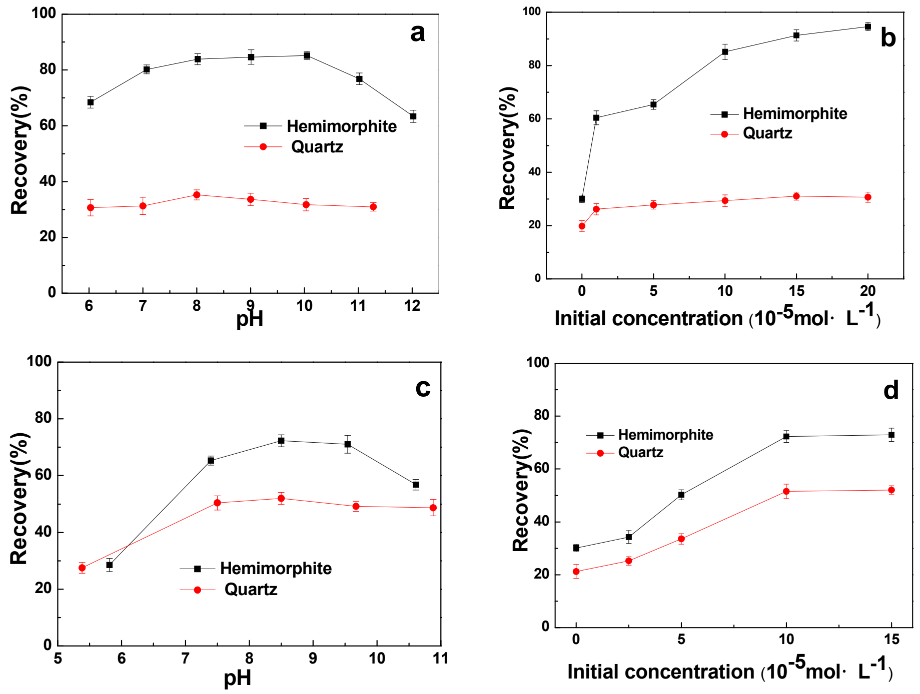

Figure 2. Flotation recovery of hemimorphite and quartz as a function of pH (under 1 × 10^{-4} mol·L^{-1} HDDPA (**a**) or lauric acid (**c**)) and initial concentration of HDDPA (**b**) or lauric acid (**d**) (under pH 8.5).

3.3. Flotation of the Artificially Mixed Minerals

As shown above, HDDPA floated out more hemimorphite than quartz. To further explore HDDPA's flotation selectivity, flotation separation tests for the artificially mixed minerals (with a 1:1 weight ratio of hemimorphite to quartz) were carried out and the experimental findings were presented in Figure 3. It could be seen from Figure 3a that the preferred pH values for the flotation recovery of hemimorphite from its mixture with quartz were 8.0–10.5 with 1.0 × 10^{-4} mol·L^{-1} HDDPA. At pH around 9.1, HDDPA floated out 76.1% hemimorphite as well as 32.3% quartz, which was slightly lower than the flotation recovery of 84.6% for hemimorphite or 33.6% for quartz in the individually pure mineral flotation tests as listed in Figure 2a. The results in Figure 3b showed that with increase of HDDPA dosage, the flotation recoveries of hemimorphite increased and those of quartz increased very slightly. At 2.0 × 10^{-4} mol·L^{-1} HDDPA, the recovery of hemimorphite or quartz reached 83.3% or 34.2%, respectively. The flotation results of the artificially mixed minerals recommended that an efficient flotation separation of hemimorphite from quartz could be reached by using HDDPA as a collector.

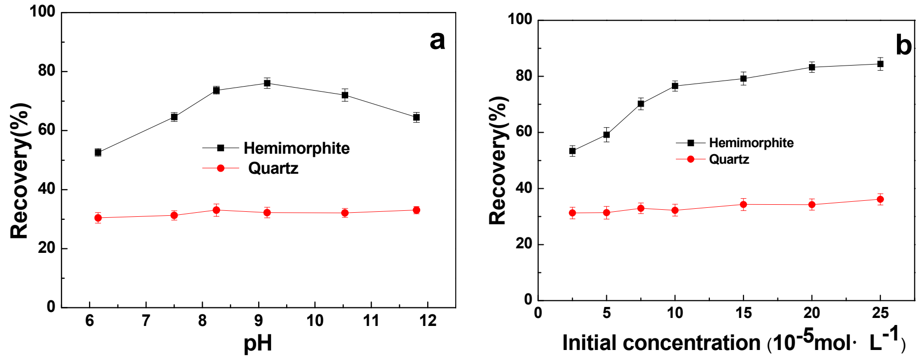

Figure 3. Flotation separation of artificially mixed minerals under different (**a**) pH (under 1.0 × 10^{-4} mol·L^{-1} HDDPA) and (**b**) initial concentration of HDDPA (at pH 8.5).

3.4. Contact Angle Results

Contact angle is an important parameter for evaluation of the wettability of mineral surfaces, which is the most intuitive sign of mineral surface hydrophobicity [39].

The contact angles of hemimorphite or quartz surfaces before and after 5 × 10^{-5} mol·L^{-1} HDDPA treatment are shown in Figure 4. It demonstrated that the contact angle of the clean hemimorphite surfaces was 42.0 ± 1.3°. After HDDPA treatment of 2 min and 5 min, hemimorphite contact angle increased to 67.8 ± 1.4° and 88.1 ± 1.5°, respectively. However, the fresh quartz surface was hydrophilic and its contact angle was maintained at about 14° before and after HDDPA treatment. This difference illustrated that HDDPA preferred to adsorb on hemimorphite rather than on quartz.

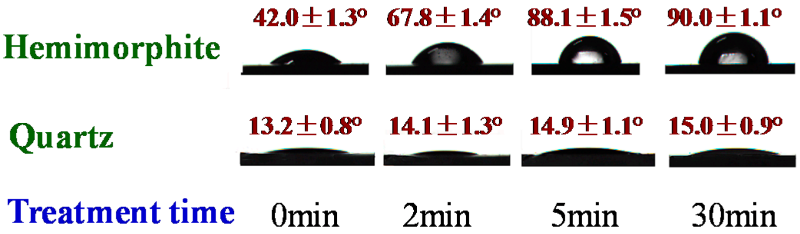

Figure 4. Contact angles of hemimorphite or quartz surfaces as a function of treatment time at 5 × 10^{-5} mol·L^{-1} HDDPA.

The contact angle of hemimorphite or quartz as a function of pH under 5 × 10^{-5} mol·L^{-1} HDDPA treatment for 5 min is shown in Figure 5. It elucidated that the contact angles of hemimorphite were slightly larger at pH 7.0–9.8 than under acidic or strong alkaline conditions, while the pH values had an insignificant effect on the contact angle of quartz under pH 6.0–11.0. The contact angle results were further confirmed by the selective hydrophobization of HDDPA to hemimorphite, which corresponded to its selective flotation to hemimorphite against quartz as presented in Figure 2a,b and Figure 3.

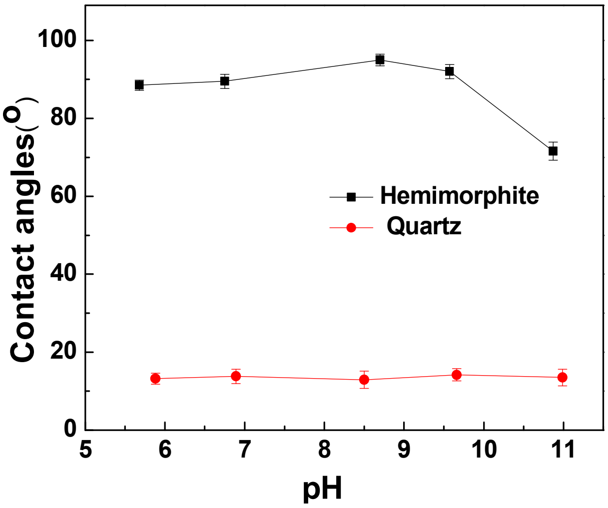

Figure 5. Contact angles of hemimorphite or quartz surfaces as a function of pH under 5 × 10^{-5} mol·L^{-1} HDDPA.

3.5. Zeta Potential Results

The zeta potential of hemimorphite particles as a function of pH in the absence or presence of 1 × 10^{-4} mol·L^{-1} HDDPA is shown in Figure 6a. It elucidated that the isoelectric point (IEP) of hemimorphite particles occurred at pH ~6.0, which was consistent with the previous reported value of pH 6.0 [40]. In the presence of HDDPA, the zeta potential of hemimorphite particles transferred to more negative values, and the IEP shifted to pH~5.1, which implied that HDDPA species might attach on to the positively charged sites of hemimorphite particles to lessen their zeta potential.

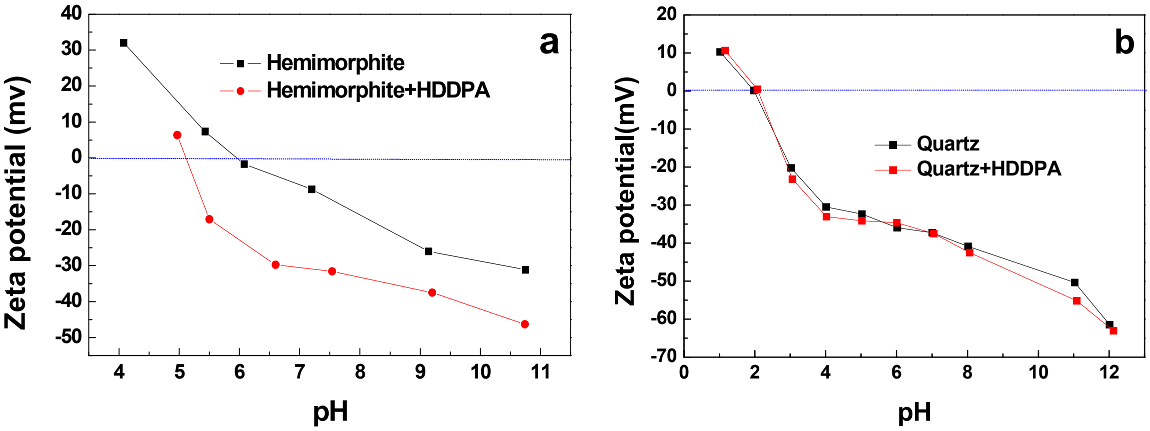

Figure 6. Zeta potential of hemimorphite (**a**) or quartz (**b**) as a function of pH in the absence and presence of 1 × 10^{-4} mol·L^{-1} HDDPA.

The zeta potential values of quartz particles with or without of 1 × 10^{-4} mol·L^{-1} HDDPA are shown in Figure 6b. The IEP of quartz particles occurred at pH 2.0, similar to what was previously measured at pH 2.2 [41]. In the presence of HDDPA, the zeta potential of quartz particles barely changed, which implied that HDDPA species hardly adsorbed on to quartz surfaces.

3.6. FTIR Analyses

The FTIR spectra of HDDPA and its precipitates with Zn^{2+} are presented in Figure 7a. For HDDPA, the characteristic peaks at around 3540 and 3228 cm^{-1} were attributed to its O–H vibrations for intramolecular and intermolecular hydrogen bonds [42]. The vibrations of C–H bonds appeared at about 2960, 2920, 2850 and 1470 cm^{-1}. The bands at around 2240 cm^{-1} were assigned to the stretching vibration of PO–H [43]. The absorption peaks at 1060 and 922 cm^{-1} represented the symmetric and asymmetric stretching vibrations of –P–O– bonds in the –P(=O)OH groups and those at around 1290 and 1160 cm^{-1} were related to the P=O and the P=O in condition of hydrogen bond [37,42,44], respectively. After reaction with Zn^{2+}, the –P–O– absorption peak at 922 cm^{-1} for HDDPA dramatically weakened and shifted to 960 cm^{-1}, and that at 1060 cm^{-1} moved to 1080 cm^{-1} in the Zn-HDDPA precipitates, suggesting the formation of the P–O–Zn bond [45]. Additionally, the peaks at around 1160, 1290, 2240, 3228 and 3540 cm^{-1} for HDDPA almost disappeared. These changes suggested that the P=O and –P–OH groups might react with Zn^{2+} and the previously existed O–H and P=O bonds might be broken (P=O was changed to P–O), which was consistent with previous reports that the oxygen atoms in both of P=O and –P–OH groups could combine with zinc atoms [36,37,46,47].

The FTIR spectra of hemimorphite before and after HDDPA adsorption are illustrated in Figure 7b. Compared with clean mineral particles, the appearance of the –C–H peaks at 2920, 2850 and 1470 cm^{-1} implied the adsorption of HDDPA on hemimorphite surfaces. Other characteristic bands at around 1080 and 960 cm^{-1} due to the P–O–Zn bonds might be covered by the strong and wide adsorption bands of hemimorphite. Additionally, the bands near 1635 and 3446 cm^{-1} as presented in Figure 7 were assigned to the O–H bending and stretching vibrations of water molecules.

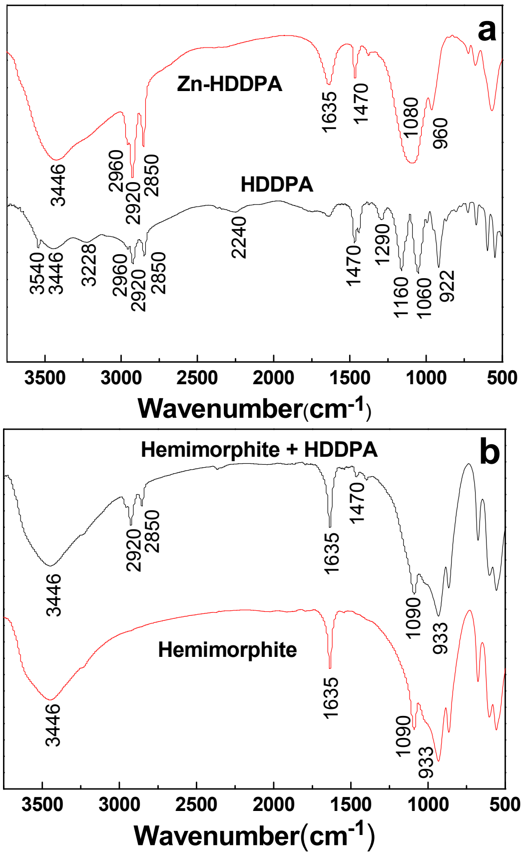

Figure 7. Fourier transform infrared (FTIR) spectra of HDDPA and Zn-HDDPA precipitate (**a**), hemimorphite before and after HDDPA adsorbed (**b**).

3.7. XPS Analyses

3.7.1. Survey XPS

The survey scan XPS of HDDPA, Zn-HDDPA precipitates, hemimorphite before and after HDDPA treatment are displayed in Figure 8, and the atomic concentrations for elements C 1s, O 1s, P 2p, Si 2p and Zn 2p are presented in Table 2. The results elucidated that the atomic proportion of carbon, oxygen and phosphorus in HDDPA was in accordance with its molecular composition of $C_{12}H_{28}P_2O_7$. For the Zn-HDDPA precipitate, the atomic ratio of phosphorus to zinc was 1.17:1, inferring that the configuration of the Zn-HDDPA precipitate might be $(HDDPA)Zn_2$ [46,47]. After HDDPA treatment, the atomic concentrations of carbon and phosphorus on hemimorphite surfaces increased and those of oxygen, silicon and zinc decreased, confirming the adsorption of HDDPA on hemimorphite.

Table 2. Atomic concentration of elements as determined by X-ray photoelectron spectroscopy (XPS).

Species	**Atomic Concentration/%**				
	C 1s	**O 1s**	**Si 2p**	**P 2p**	**Zn 2p**
HDDPA	59.24	30.69	-	9.87	-
Zn-HDDPA precipitate	57.11	27.49	-	8.31	7.09
Hemimorphite	9.79	54.02	12.46	-	23.73
Hemimorphite after HDDPA treatment	39.12	41.74	5.51	3.44	10.19

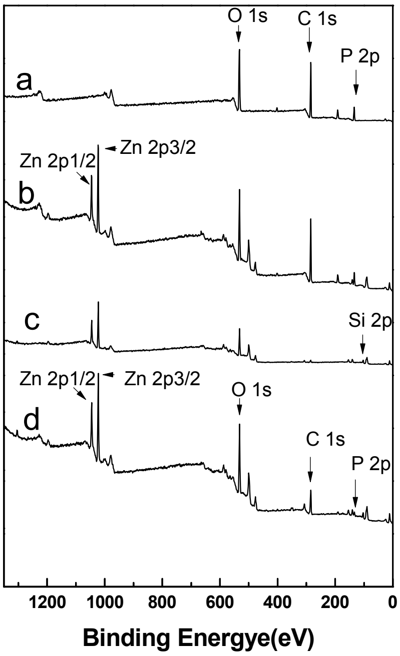

Figure 8. The X-ray photoelectron spectroscopy (XPS) survey scan of HDDPA (**a**) and Zn-HDDPA precipitates (**b**), hemimorphite without (**c**) or with (**d**) HDDPA treatment.

3.7.2. High-Resolution XPS

The high-resolution XPS of Zn 2p and P 2p and for HDDPA, Zn-HDDPA precipitates, hemimorphite with or without HDDPA treatment are shown in Figure 9. The results in Figure 9a illustrated that the Zn $2p_{3/2}$ XPS peak of hemimorphite appeared at around 1022.14 eV [48] and that of the Zn-HDDPA precipitate emerged on 1022.68 eV [49]. After HDDPA treatment, the Zn $2p_{3/2}$ XPS bands of hemimorphite were composed of two components at around 1022.12 and 1022.76 eV. The low binding energy peak was assigned to the inner-layer Zn(II) species of hemimorphite interface [48,49], the high binding energy peak might be due to the Zn(II) surface species which combined with HDDPA. This inferred that hemimorphite might chemosorb HDDPA on its surfaces [29].

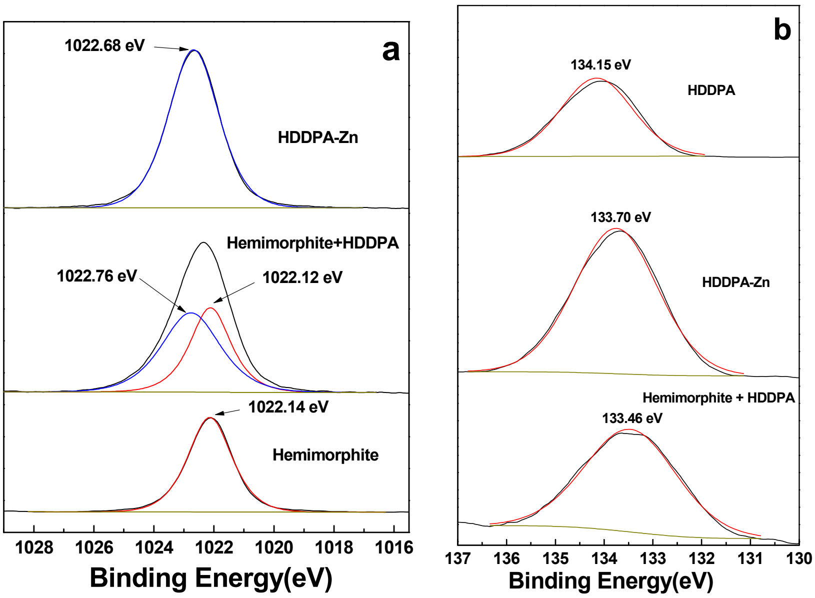

Figure 9. High-resolution XPS of Zn 2p3/2 (**a**) and P 2p (**b**).

Figure 9b illustrated that the P 2p XPS bands occurred at around 134.15 eV for HDDPA, 133.70 eV for the Zn-HDDPA precipitate and 133.46 eV for HDDPA adsorbed on hemimorphite surfaces, which elucidated that after HDDPA reaction with Zn ions or adsorption on hemimorphite surfaces, the P 2p binding energy decreased, suggesting that HDDPA might chemisorb on to hemimorphite surfaces to increase the electron density around the P atom [50]. The increased binding energy for Zn $2p_{3/2}$ and the reduced for P 2p confirmed that the Zn(II)-HDDPA surface complexes might be formed on hemimorphite [46,47].

4. Discussion

The micro-flotation findings showed that HDDPA displayed superior flotation performance to hemimorphite in comparison with lauric acid and good selectivity against quartz flotation under pH 7.0–11.0. The contact angle results displayed that HDDPA preferred to adsorb on to hemimorphite rather than quartz and promoted the hydrophobicity of hemimorphite surfaces.

The pK_{a1}, pK_{a2}, pK_{a3} and pK_{a4} (K_a is defined as an acid dissociation constant) of 1-hydroxyoctylidene-1,1-diphosphonic acid were 1.56, 3.00, 7.03 and 11.01 [37], respectively. This means that HDDPA mainly existed in aqueous solutions as HDDPA at pH $\leq$ 1.5, $HDDPA^{-}$ at pH 1.5–3.0, $HDDPA^{2-}$ at pH 3.0–7.0, $HDDPA^{3-}$ at pH 7.0–11.0 or $HDDPA^{4-}$ at pH $\geq$ 11.0.

The IEP of hemimorphite particles occurred at pH around 6.0. Under pH > 6.0, HDDPA mainly exists as its negatively charged species and hemimorphite particles might be negatively charged. The zeta potential results indicated that HDDPA species did adsorb on hemimorphite at pH > 6.0, implying that HDDPA might chemisorb on to hemimorphite surfaces, which can conquer the electrostatic repulsion interaction between them.

The FTIR recommended that HDDPA might anchor on hemimorphite surfaces through bonding the oxygen atoms in its P(=O)–O group with surface Zn(II) species [48,49]. The P 2p and Zn $2p_{3/2}$ XPS gave clear evidence that HDDPA anchored on hemimorphite surfaces by chemisorption. Thus, Zn(II)-HDDPA surface complexes might be formed on hemimorphite [46,47], which hydrophobized hemimorphite particles to be floated out in froth flotation.

Hemimorphite ($Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$) might dissolve in water according to Equation 4 [51]. Medusa was adopted to evaluate the concentration of Zn or Si species from hemimorphite as a function of pH; the plot is presented in Figure 10. It demonstrated that in acidic solutions, Zn^{2+} ions dominate in water, and under pH > 11.5, Zn species mainly exists as $Zn(OH)_2$, $Zn(OH)_3{}^{-}$ and $ZnSiO_3$.

$$Zn_4(Si_2O_7)(OH)_2 \cdot H_2O(s) \rightleftharpoons 2SiO_3{}^{2-} + 4Zn^{2+} + 4OH^{-} \quad (4)$$

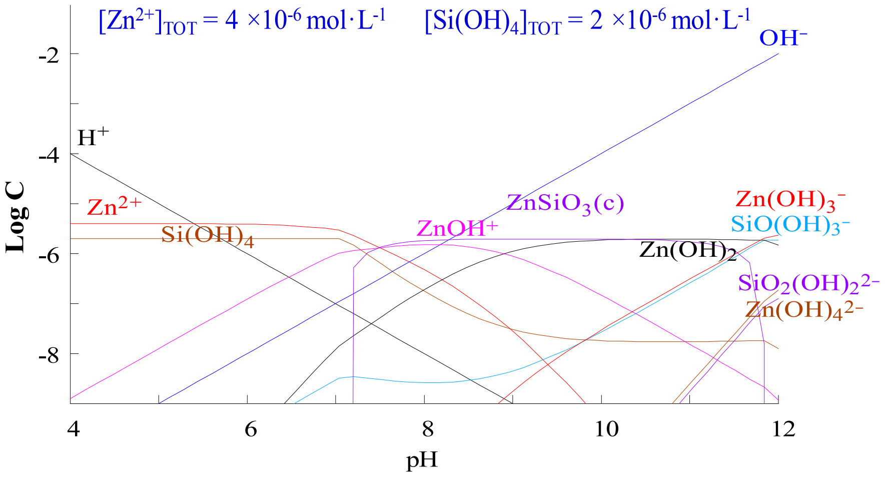

Figure 10. Zn or Si species of hemimorphite in water.

Under pH 7.0–11.0, HDDPA mainly exists as $HDDPA^{3-}$ species in aqueous solutions, $Zn(OH)_2$ and $ZnSiO_3$ might be the main Zn species on hemimorphite surfaces, and some $ZnOH^+$ species would be adsorbed on to hemimorphite surfaces. Therefore, $HDDPA^{3-}$ might react with Zn(II) species of hemimorphite surfaces to form Zn(II)-HDDPA surface complexes. In acidic conditions, the dissolved Zn^{2+} ions would combine with $HDDPA^{2-}$ ions to reduce $HDDPA^{2-}$ adsorption towards hemimorphite, resulting in a descended flotation recovery of hemimorphite. Under pH > 11.0, the adsorption of $Zn(OH)_3{}^-$ or $SiO(OH)_3{}^-$ on to hemimorphite surfaces would increase, and $HDDPA^{4-}$ adsorption to hemimorphite might face strong electrostatic repulsion between them, which also rendered a rapidly reduced flotation recovery of hemimorphite.

5. Conclusions

In this paper, 1-hydroxydodecylidene-1,1-diphosphonic acid (HDDPA) was prepared and introduced as a collector for hemimorphite flotation. Based on the experimental findings and analyses, we could draw the following conclusions:

HDDPA exhibited good performances for flotation recovery of hemimorphite in comparison with lauric acid, and it also possessed good selectivity against quartz flotation under pH 7.0–11.0. Contact angle results revealed that HDDPA selectively adsorbed on to hemimorphite rather than quartz and dramatically improved hemimorphite hydrophobicity. In the presence of HDDPA anions, the zeta potential of hemimorphite particles moved to more negative values, inferring a strong chemisorption of HDDPA on to hemimorphite. The FTIR recommended that HDDPA anchored on hemimorphite surfaces through bonding the oxygen atoms of its P(=O)–O groups with surface Zn(II) species. XPS gave additional evidence that Zn(II)-HDDPA surface complexes were formed on hemimorphite.

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References

1. Seifert, S.; Simon, F.; Baumann, G.; Hietschold, M.; Seifert, A.; Spange, S. Adsorption of poly(vinyl formamide-co-vinyl amine) (PVFA-co-PVAm) polymers on zinc, zinc oxide, iron, and iron oxide surfaces. *Langmuir* **2011**, *27*, 14279–14289. [CrossRef] [PubMed]
2. Fogliatti, D.P.; Kemppainen, S.A.; Kalnes, T.N.; Fan, J.; Shonnard, D.R. Life cycle carbon footprint of linear alkylbenzenesulfonate from coconut oil, palm kernel oil, and petroleum-based paraffins. *ACS Sustain. Chem. Eng.* **2014**, *2*, 1828–1834. [CrossRef]
3. Harvey, T.J.; Yen, W.T. The influence of chalcopyrite, galena and pyrite on the selective extraction of zinc from base metal sulphide concentrates. *Miner. Eng.* **1998**, *11*, 1–21. [CrossRef]
4. Wu, X.Q.; Zhu, J.G. Selective flotation of cassiterite with benzohydroxamic acid. *Miner. Eng.* **2006**, *19*, 1410–1417. [CrossRef]
5. Huang, Z.; Zhong, H.; Wang, S.; Xia, L.; Zou, W.; Liu, G. Investigations on reverse cationic flotation of iron ore by using a gemini surfactant: Ethane-1,2-bis(dimethyl-dodecyl-ammonium bromide). *Chem. Eng. J.* **2014**, *257*, 218–228. [CrossRef]
6. Fairthorne, G.; Brinen, J.S.; Fornasiero, D.; Nagaraj, D.R.; Ralston, J. Spectroscopic and electrokinetic study of the adsorption of butyl ethoxycarbonyl thiourea on chalcopyrite. *Int. J. Miner. Process.* **1998**, *54*, 147–163. [CrossRef]
7. Güler, T.; Hiçyilmaz, C.; Gökagˇ Aç, G.; Ekmeçi, Z. Adsorption of dithiophosphate and dithiophosphinate on chalcopyrite. *Miner. Eng.* **2006**, *19*, 62–71. [CrossRef]
8. Bulatovic, S.M. *Handbook of Flotation Reagents*; Elsevier Science: Amsterdam, The Netherlands, 2010; Volume 2, p. 68. ISBN 978-04-4-453082-0.

9. Irannajad, M.; Ejtemaei, M.; Gharabaghi, M. The effect of reagents on selective flotation of smithsonite–calcite–quartz. *Miner. Eng.* **2009**, *22*, 766–771. [CrossRef]
10. Mehdilo, A.; Zarei, H.; Irannajad, M.; Arjmandfar, H. Flotation of zinc oxide ores by cationic and mixed collectors. *Miner. Eng.* **2012**, *36–38*, 331–334. [CrossRef]
11. Keqing, F.A.; Miller, J.D.; Jiang, T.; Li, G. Sulphidization flotation for recovery of lead and zinc from oxide-sulfide ores. *Trans. Nonferrous Met. Soc. China* **2005**, *15*, 1138–1144.
12. Liu, C.; Feng, Q.; Zhang, G.; Ma, W.; Meng, Q.; Chen, Y. Effects of lead ions on the flotation of hemimorphite using sodium oleate. *Miner. Eng.* **2016**, *89*, 163–167. [CrossRef]
13. Wang, Q.; Zhang, X.; Jing, M.; Rao, F.; Wu, L.; Li, K.; Cao, S. A review of forming process and flotation mechanism of hemimorphite. *Chin. J. Process Eng.* **2017**, *17*, 903–910. [CrossRef]
14. Hosseini, S.H.; Forssberg, E. Adsorption studies of smithsonite flotation using dodecylamine and oleic acid. *Miner. Metall. Process.* **2006**, *23*, 87–96.
15. Ejtemaei, M.; Irannajad, M.; Gharabaghi, M. Influence of important factors on flotation of zinc oxide mineral using cationic, anionic and mixed (cationic/anionic) collectors. *Miner. Eng.* **2011**, *24*, 1402–1408. [CrossRef]
16. Hosseini, S. Selective flotation of angooran oxidised zinc ore using mercaptans. In Proceedings of the International Mineral Processing Symposium, Belek-Antalya, Turkey, 21–23 October 2008; Turkish Mining Development Foundation: Ankara, Turkey, 2008; pp. 367–376.
17. Marabini, A.M.; Ciriachi, M.; Plescia, P.; Barbaro, M. Chelating reagents for flotation. *Miner. Eng.* **2007**, *20*, 1014–1025. [CrossRef]
18. Han, C.; Wei, D.Z.; Shen, Y.B.; Liu, W.G. Flotation behavior of hemimorphite and smithsonite in dodecylamine system. *J. Northeast. Univ. Nat. Sci.* **2016**, *37*, 1582–1587. [CrossRef]
19. Ejtemaei, M.; Gharabaghi, M.; Irannajad, M. A review of zinc oxide mineral beneficiation using flotation method. *Adv. Colloid Interface Sci.* **2014**, *206*, 68–78. [CrossRef] [PubMed]
20. Grimm, R.; Kolařík, Z. Acidic organophosphorus extractants-XIX: Extraction of Cu(II), Ni(II), Zn(II) and Cd(II) by di(2-ethylhexyl) phosphoric acid. *J. Inorg. Nucl. Chem.* **1974**, *36*, 189–192. [CrossRef]
21. Owusu, G. Selective extractions of Zn and Cd from Zn-Cd-Co-Ni sulphate solution using di-2-ethylhexyl phosphoric acid extractant. *Hydrometallurgy* **1998**, *47*, 205–215. [CrossRef]
22. Miralles, N.; Sastre, A.M. Comparative study of the distribution equilibria of Zn(II) in chloride medium by organophosphoric,-phosphonic and -phosphinic acids. *Monatsh. Chem.* **1993**, *124*, 987–994. [CrossRef]
23. Sainz-Diaz, C.I.; Klocker, H.; Marr, R.; Bart, H.J. New approach in the modelling of the extraction equilibrium of zinc with bis-(2-ethylhexyl) phosphoric acid. *Hydrometallurgy* **1996**, *42*, 1–11. [CrossRef]
24. Liu, Q.; Peng, Y. The development of a composite collector for the flotation of rutile. *Miner. Eng.* **1999**, *12*, 1419–1430. [CrossRef]
25. Gruner, H.; Bilsing, U. Cassiterite flotation using styrene phosphonic acid to produce high-grade concentrates at high recoveries from finely disseminated ores- comparison with other collectors and discussion of effective circuit configurations. *Miner. Eng.* **1992**, *5*, 429–434. [CrossRef]
26. Li, F.; Zhong, H.; Zhao, G.; Wang, S.; Liu, G. Flotation performances and adsorption mechanism of α-hydroxyoctyl phosphinic acid to cassiterite. *Appl. Surf. Sci.* **2015**, *353*, 856–864. [CrossRef]
27. Li, F.; Zhong, H.; Xu, H.; Jia, H.; Liu, G. Flotation behavior and adsorption mechanism of α-hydroxyoctyl phosphinic acid to malachite. *Miner. Eng.* **2015**, *71*, 188–193. [CrossRef]
28. Li, F.; Zhong, H.; Wang, S.; Liu, G. The activation mechanism of Cu(II) to ilmenite and subsequent flotation response to α-hydroxyoctyl phosphinic acid. *Ind. Eng. Chem.* **2016**, *37*, 123–130. [CrossRef]
29. Li, F.; Zhong, H.; Zhao, G.; Wang, S.; Liu, G. Adsorption of α-hydroxyoctyl phosphonic acid to ilmenite/water interface and its application in flotation. *Colloids Surf. A* **2016**, *490*, 67–73. [CrossRef]
30. Jurisson, S.; Berning, D.; Jia, W.; Ma, D. Coordination compounds in nuclear medicine. *Chem. Rev.* **1993**, *93*, 1137–1156. [CrossRef]
31. Rizkalla, E.N.; Zaki, M.T.; Ismail, M.I. Metal chelates of phosphonate-containing ligands-V stability of some 1-hydroxyethane-1,1-diphosphonic acid metal chelates. *Talanta* **1980**, *27*, 715–719. [CrossRef]
32. Kotlyarevsky, I.L.; Alferiev, I.S.; Krasnukhina, A.V.; Pomazov, V.D.; Egorov, N.V. New phospho-organic collectors for flotation of non-sulphide minerals. In *Reagents in Mineral Technology*; Jones, M.J., Oblatt, R., Eds.; Institution of Mining and Metallurgy: London, UK, 1984; pp. 173–179, ISBN 978-08-2-477715-9.
33. Houot, R. Is the cassiterite contained in complex sulphide polymetallic ore recoverable? *Int. J. Miner. Process.* **1991**, *32*, 45–57. [CrossRef]

34. Lavrinenko, A.A.; Shrader, E.A.; Kharchikov, A.N.; Kunilova, I.V. Apatite flotation from brazilite-apatite-magnetite ore. *J. Min. Sci.* **2013**, *49*, 811–818. [CrossRef]
35. Chaudhuri Pradip, N.C. Flotation of degana wolframite. *Trans. Indian Inst. Met.* **1997**, *50*, 383–390.
36. Chen, G.L.; Tao, D.; Ren, H.; Ji, F.F.; Qiao, J.K. An investigation of niobite flotation with octyl diphosphonic acid as collector. *Int. J. Miner. Process.* **2005**, *76*, 111–122. [CrossRef]
37. Zheng, X.P.; Misra, M.; Smith, R.W.; Qiao, J.K. Fersmite flotation with diphosphonic acid and other collectors. *Miner. Eng.* **1996**, *9*, 331–341. [CrossRef]
38. Kieczykowski, G.R.; Jobson, R.B.; Melillo, D.G.; Reinhold, D.F.; Grenda, V.J.; Shinkai, I. Preparation of (4-amino-1-hydroxybutylidene)bisphosphonic acid sodium salt, MK-217 (alendronate aodium). An improved procedure for the preparation of 1-hydroxy-1,1-bisphosphonic acids. *J. Org. Chem.* **1995**, *27*, 8310–8312. [CrossRef]
39. Ozdemir, O.; Karaguzel, C.; Nguyen, A.V.; Celik, M.S.; Miller, J.D. Contact angle and bubble attachment studies in the flotation of trona and other soluble carbonate salts. *Miner. Eng.* **2009**, *22*, 168–175. [CrossRef]
40. Pereira, C.A.; Peres, A.E.C. Reagents in calamine zinc ores flotation. *Miner. Eng.* **2005**, *18*, 275–277. [CrossRef]
41. Abaka-Wood, G.B.; Addai-Mensah, J.; Skinner, W. A study of flotation characteristics of monazite, hematite and quartz using anionic collectors. *Int. J. Miner. Process.* **2016**, *158*, 55–62. [CrossRef]
42. Jingzun, W.; Ting, W. How to explain the infrared spectrum. *Univ. Chem.* **2016**, *31*, 90–97. [CrossRef]
43. Elias, A.; Didi, M.A.; Villemin, D.; Semaoune, T.; Ouattas, S. Synthesis of mono-and dialkylphosphates by the reactions of hydroxycompounds with the phosphorus pentaoxide under microwave irradiation. *Phosphorus Sulfur Silicon Relat. Elem.* **2004**, *179*, 2599–2607. [CrossRef]
44. Ren, H.; Ji, F.; Zhang, S. Effect and mechanism of diphosphonic acid on flotation characteristic of fersmite and intergrowth gangue. *Trans. Nonferrous Met. Soc. China* **2003**, *13*, 1013–1018.
45. Andrews, B.; Almahdali, S.; James, K.; Ly, S.; Crowder, K.N. Copper oxide surfaces modified by alkylphosphonic acids with terminal pyridyl-based ligands as a platform for supported catalysis. *Polyhedron* **2016**, *114*, 360–369. [CrossRef]
46. Chausov, F.F. Structurally selective protection of steel against oxygen corrosion by 1-hydroxyethylidenediphosphonatozincate. *Bull. Russ. Acad. Sci. Phys.* **2013**, *77*, 324–326. [CrossRef]
47. Fu, R.B.; Hu, S.M.; Wu, X.T. Luminescent zinc phosphonates for ratiometric sensing of 2,4,6-trinitrophenol and temperature. *Cryst. Growth Des.* **2016**, *16*, 5074–5083. [CrossRef]
48. Pilbáth, A.; Nyikos, L.; Bertóti, I.; Kálmán, E. Zinc corrosion protection with 1,5-diphosphono-pentane. *Corros. Sci.* **2008**, *50*, 3314–3321. [CrossRef]
49. Pilbáth, A.; Bertóti, I.; Pfeifer, É.; Mink, J.; Nyikos, L.; Kálmán, E. Formation and characterization of 1, 5-diphosphono-pentane films on polycrystalline zinc substrates. *Surf. Coat. Technol.* **2009**, *203*, 1182–1192. [CrossRef]
50. Ren, H.; Ji, F.; Zhang, S.; Bao, M.; Zhang, Q. Effects of diphosphonic acid on ilmenorutile collecting property and research of action mechanism. *J. Univ. Sci. Technol. Beijing* **2002**, *9*, 249–252.
51. Chen, A.; Li, M.; Qian, Z.; Ma, Y.T.; Che, J.; Ma, Y.L. Hemimorphite ores: A review of processing technologies for zinc extraction. *J. Miner. Met. Mater. Soc.* **2016**, *68*, 2688–2697. [CrossRef]